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最終頁に続く

(54)【発明の名称】　モンモリロナイト型の大きな格子間距離を有する橋状２：１ジ八面体フィロシリケート、触媒および転換方法

(57)【要約】
【課題】　活性化された天然の、または合成により得られるモンモリロナイト型２：１ジ八面体フィロシリケートを提供する。
【解決手段】　少なくとも２．００×１０$^{-9}$ｍの格子間距離を有し、かつSiO_2、Al_2O_3、TiO_2、ZrO_2およびV_2O_5からなる群から選ばれる化合物のうちの少なくとも１つの化合物、あるいはこれら化合物のあらゆる組み合わせをベースとする柱を層間スペース内に含むモンモリロナイト型２：１ジ八面体フィロシリケートである。

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【特許請求の範囲】

【請求項1】　少なくとも2．00×10^{-9}mの格子間距離を有し、かつSiO_2、Al_2O_3、TiO_2、ZrO_2およびV_2O_5からなる群から選ばれる化合物のうちの少なくとも1つの化合物、あるいはこれら化合物のあらゆる組み合わせをベースとする柱を層間スペース内に含むモンモリロナイト型2：1ジ八面体フィロシリケート。

【請求項2】　フッ素を含む請求項1記載の2：1ジ八面体フィロシリケート。

【請求項3】　格子間距離が少なくとも2．65×10^{-9}mである、請求項1または2記載の2：1ジ八面体フィロシリケート。

【請求項4】　格子間距離が少なくとも3．0×10^{-9}mである、請求項1～3のうちのいずれか1項記載の2：1ジ八面体フィロシリケート。

【請求項5】　格子間距離が少なくとも3．3×10^{-9}mである、請求項1～4のうちのいずれか1項記載の2：1ジ八面体フィロシリケート。

【請求項6】　格子間距離が多くとも6．0×10^{-9}mである、請求項1～5のうちのいずれか1項記載の2：1ジ八面体フィロシリケート。

【請求項7】　柱SiO_2を含む、請求項1～6のうちのいずれか1項記載の2：1ジ八面体フィロシリケート。

【請求項8】　SiO_2と、Al_2O_3、TiO_2、ZrO_2およびV_2O_5からなる群から選ばれる化合物のうちの少なくとも1つの化合物との組合わせをベースとする柱を含む、請求項1～7のうちのいずれか1項記載の2：1ジ八面体フィロシリケート。

【請求項9】　フィロシリケートが界面活性剤の溶液中において懸濁化され、次いで溶液から固体を分離した後に、フィロシリケートが、少なくとも1つの第1または第2アミンと、Si、Al、Zr、TiおよびVからなる群から選ばれる元素の少なくとも1つのアルコキシドとを含む混合物と接触される、少なくとも2．00×10^{-9}mの格子間距離を有する2：1ジ八面体フィロシリケートの調製方法。

【請求項10】　懸濁状にされたフィロシリケートが、アンモニウム（NH_4^+）型である、請求項9記載の方法。

【請求項11】　界面活性剤の溶液が、0．01～1モル／リットルの濃度を有する、請求項9または10記載の方法。

【請求項12】　第1アミンRNH_2または第2アミンR'RNHが、アルキル、イソ・アルキル、ナフテニルおよび置換または非置換芳香族基からなる群から選ばれる炭素原子数1～16のR基およびR'基を有し、また元素Mのアルコキシド$M(OR)_n$が、アルキル、イソ・アルキル、ナフテニルおよび置換または非置換芳香族基からなる群から選ばれる炭素原子数1～16のR基を有する、請求項9～11のうちのいずれか1項記載の方法。

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【請求項13】　請求項1～8のうちのいずれか1項記載の、または請求項9～12のうちのいずれか1項記載により調製される少なくとも1つの2：1ジ八面体フィロシリケートと、少なくとも1つのマトリックスと、場合によってはゼオライトYとを含む触媒。

【請求項14】　請求項9～12のうちのいずれか1項記載により調製される少なくとも1つの2：1ジ八面体フィロシリケートと、少なくとも1つのマトリックスと、場合によってはゼオライトYとを含む触媒。

【請求項15】・少なくとも1つの2：1ジ八面体フィロシリケート　1～80重量%と、
・少なくとも1つのゼオライトY　0～30重量%と、
・少なくとも1つのマトリックス　1～99重量%と
を含む、請求項13または14記載の触媒。

【請求項16】　さらに少なくとも1つの触媒元素を含む、請求項13～15のうちのいずれか1項記載の触媒。

【請求項17】　触媒元素が、水素化・脱水素化元素である、請求項16記載の触媒。

【請求項18】　さらに燐を含む、請求項13～17のうちのいずれか1項記載の触媒。

【請求項19】　マトリックスが、アルミナ、シリカ、酸化マグネシウム、酸化チタン、酸化ジルコニウム、燐酸チタン、燐酸ジルコニウムおよび酸化ホウ素からなる群から選ばれる、請求項13～18のうちのいずれか1項記載の触媒。

【請求項20】　フッ素を含む2：1ジ八面体フィロシリケートを含む、請求項13～19のうちのいずれか1項記載の触媒。

【請求項21】　脱アルミニウムゼオライトYを含む、請求項13～20のうちのいずれか1項記載の触媒。

【請求項22】　請求項13～21のうちのいずれか1項記載の触媒を用いる炭化水素転換方法。

【請求項23】　さらに少なくとも1つの水素化・脱水素化元素を含む触媒を用いる水素化クラッキングにおける請求項22記載の方法。

【請求項24】　温度230℃以上、圧力少なくとも2MPaおよびVVH0．2～10h^{-1}で操作を行う、請求項23記載の方法。

【請求項25】　ガスオイル、減圧ガスオイル、脱アスファルト残渣または水素化処理済み残渣について操作を行う、請求項23または24記載の方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、例えば活性化された天然の、または合成により得られるモンモリロナイト型2：1ジ八面体フィロシリケートに関する。前記合成

は、場合によってはフッ化水素酸および／または別のフッ化物アニオン源の存在下にフッ化物媒質中において行われる。前記フィロシリケートは、橋状(bridged) でありかつ大きな格子間距離(interplanar spacing) を有する。d001 により表される格子間距離は、層（シート）の厚みと層間スペースとの合計である。

【0002】さらに本発明は、前記フィロシリケートを得るための調製方法にも関する。

【0003】これらフィロシリケートは、炭化水素仕込原料の水素化クラッキングにおいて使用される触媒の組成物中に含まれてよい。

【0004】さらに本発明は、例えば活性化された天然の、すなわち例えば酸で処理された、あるいは場合によってはフッ化物媒質中で（フッ化水素酸および／または別のフッ化物アニオン源の存在下に）合成され、ついで橋状化された少なくとも１つのモンモリロナイト型２：１ジ八面体フィロシリケートを含む触媒にも関する。前記フィロシリケートは、大きな格子間距離（この格子間距離は、層（sheet シート）の厚みと層間スペース(space between the sheets)との合計である）を有する。さらに触媒は、少なくとも１つのマトリックスと、場合によっては少なくとも１つのフォージャサイト構造型ゼオライトYとを含む。さらに本発明は、この触媒を用いる炭化水素仕込原料の転換方法、特に水素化クラッキング方法にも関する。

【0005】

【従来の技術】重質石油留分の水素化クラッキングは、石油精製の非常に重要な方法であり、この精製方法により、ほとんど付加価値のない余剰の重質仕込原料からガソリン、気化燃料および軽質ガスオイルのような軽質フラクションを製造することが可能になる。これらの軽質フラクションは、その製造を市場の需要に適合させるために精油業者によって探求されるものである。接触クラッキングに比して、接触水素化クラッキングのメリットは、非常に高品質の中間留分、気化燃料（ジェット燃料）およびガスオイルを供給することである。これに対して、生成されたガソリンは、接触クラッキングにより生じたガソリンよりもかなり低いオクタン価を有する。

【0006】水素化クラッキングにおいて使用される触媒は、酸機能と水素化機能とを組み合わせる二元機能型のあらゆる触媒である。酸機能は、表面酸度を有する大きな比表面積（一般に１５０～８００m^2 ／ｇ）の担体、例えばハロゲン化（特に塩素化またはフッ素化）アルミナ、酸化ホウ素とアルミニウムとの組み合わせ、非晶質シリカ・アルミナおよびゼオライトによりもたらされる。水素化機能は、元素周期表第VIII族の１つまたは複数の金属、例えば鉄、コバルト、ニッケル、ルテニウム、ロジウム、パラジウム、オスミウム、イリジウムおよび白金によるか、あるいは元素周期表第VI族の少なくとも１つの金属、例えばクロム、モリブデンおよびタングステンと第VIII族の少なくとも１つの金属との組み合わせによりもたらされる。

【0007】酸機能および水素化機能である二元機能間の平衡は、基本的なパラメータである。このパラメータにより、触媒の活性と選択性とが決定づけられる。弱酸機能と強水素化機能とにより、ほとんど活性でない（低活性度）触媒が提供される。これらの触媒は、一般に高温（３９０℃以上）で低い空間供給速度（毎時、触媒容積の１ユニット当たり処理すべき仕込原料の容積で表示されるＶＶＨが、一般に２以下である）で作用するが、これらは、中間留分の非常に高い選択性を備える。逆に、強酸機能と弱水素化機能とにより、非常に活性な触媒が提供されるが、これらは、中間留分において低い選択性を示す。従って、これらの機能の各々を適切に選択することによって、触媒の活性／選択性の一組を調整することが可能である。

【0008】従って、いくつかのレベルにおいて大きな適応性（フレキシビリティ）、すなわち使用される触媒に関しての適応性（フレキシビリティ）を有することが、水素化クラッキングの大きなメリットのうちの１つである。この適応性（フレキシビリティ）により、得られた物質に関して、処理すべき仕込原料の適応性（フレキシビリティ）がもたらされる。制御するのが容易なパラメータは、触媒担体の酸度である。

【0009】従来の接触水素化クラッキング触媒は、その大半において、弱酸性である担体、例えば非晶質シリカ・アルミナから構成される。これらの系は、非常に高品質の中間留分を製造するために、さらにはその酸度が非常に低い場合には、原料油を製造するために使用される。

【0010】非晶質シリカ・アルミナは弱酸性担体である。市場における多数の水素化クラッキング触媒は、第VIII族の金属に組み合わされたシリカ・アルミナか、あるいは好ましくは、処理すべき仕込原料のヘテロ原子毒（例えばＳ、Ｎおよび重質金属）の含有量が、０．５重量％を越える場合には、第VIB 族および第VIII族の金属の硫化物の組合わせに組み合わされたシリカ・アルミナから構成される。これらの系は、中間留分の非常に高い選択性を有する。生成された物質は、高品質を有する。さらに、それらの触媒のうちで最も弱酸性のものに関しては、そのような触媒は、潤滑原料油を製造することも可能である。非晶質担体をベースとするこれらのあらゆる触媒系の不都合は、既述したように、その弱活性度である。

【0011】

【発明の構成】本出願人により行われた研究業績により、予期しないことではあるが、少なくとも１つのモンモリロナイト型２：１ジ八面体フィロシリケートを含む触媒により、先行技術における公知触媒に比して水素化クラッキングにおける性能を改善するのが可能になるこ

とが証明されるに至った。同ジ八面体フィロシリケートは、活性化された、すなわち例えば酸で処理された天然のフィロシリケートと、あるいは場合によってはフッ化物媒質中で（フッ化水素酸ＨＦおよび／または別のフッ化物アニオン源の存在下に）合成され、ついで（好ましくは本明細書に記載される方法により）橋状化され、場合によってはフォージャサイト構造型のゼオライトＹと組み合わされる。

【００１２】より正確には、本発明は、少なくとも２．０×１０$^{-9}$ｍのd_{001}により表される格子間距離を有し、かつSiO_2、Al_2O_3、TiO_2、ZrO_2およびV_2O_5からなる群から選ばれる化合物のうちの少なくとも１つの化合物、あるいはこれらの化合物のあらゆる組み合わせをベースとする柱(pillar)を層間スペース内に含むモンモリロナイト型２：１ジ八面体フィロシリケートに関する。好ましくは、フィロシリケートは、柱SiO_2を含むか、さもなければSiO_2と、Al_2O_3、TiO_2、ZrO_2およびV_2O_5からなる群から選ばれる化合物のうちの少なくとも１つの化合物との組み合わせをベースとする柱を含む。場合によっては、該フィロシリケートは、フッ素を含む。

【００１３】本発明によれば、（場合によってはフッ化水素酸ＨＦおよび／または別のフッ化物アニオン源の存在下にフッ化物媒質中において予め調製される）これらの橋状２：１ジ八面体フィロシリケートは、少なくとも２．０×１０$^{-9}$ｍ、好ましくは少なくとも２．６５×１０$^{-9}$ｍ、より好ましくは２．８×１０$^{-9}$ｍを越える、あるいはさらには３．０×１０$^{-9}$ｍを越える格子間距離d_{001}を有する。少なくとも３．３×１０$^{-9}$ｍの距離は、特に柱SiO_2あるいは柱SiO_2＋他の酸化物において得られうる。この格子間距離は、一般に６．０×１０$^{-9}$ｍ以下、好ましくは５．０×１０$^{-9}$ｍ以下である。d_{001}により表される格子間距離は、層（シート）の厚みと層間スペースとの合計を表す。この値は、従来の配向された(orientated)粉末Ｘ線回折法を用いて直接得られうる。

【００１４】さらに本発明は、前記フィロシリケートの調製方法に関する。この方法において、フィロシリケートは、界面活性剤の溶液中において懸濁状にされ、次いで該溶液から固体を分離した後に、該フィロシリケートは、少なくとも１つの第１または第２アミンと、Ｓｉ、Ａｌ、Ｚｒ、ＴｉおよびＶからなる群から選ばれる元素の少なくとも１つのアルコキシドとを含む混合物と接触される。好ましくは、少なくとも１つのケイ素アルコキシドが、場合によってはＡｌ、Ｚｒ、ＴｉおよびＶからなる群から選ばれる元素の少なくとも１つのアルコキシドと共に使用される。

【００１５】２：１ジ八面体フィロシリケートは、元素状の層（シート）の積み重ねにより生じる鉱物である。フィロシリケート構造の元素間の化学結合は、イオン共有結合であるにも拘らず、これらの化学結合は、本明細書を簡素にするためにイオン性であると仮定される。

【００１６】イオンO^{2-}が平面において互いに接触している表示から、イオンO^{2-}の２個の配列から１個のイオンO^{2-}を取り去ることにより、六角形状面と呼ばれる、六角形状空洞（キャビティ）を有する面を得ることが可能である。

【００１７】フィライトの構造は、イオンO^{2-}の六角形状面と、イオンO^{2-}およびイオンOH^-のコンパクト面との配置によって簡単に表されうる。イオンOH^-により、イオンO^{2-}の六角形状面の空洞が満たされる。六角形状面により両側を挟まれた２つのコンパクト面の重ね合わせにより、２つの四面体層（Ｔ）の間に八面体層（Ｏ）を画定することが可能になり、このことから、層（シート）ＴＯＴの命名が由来する。

【００１８】同様に２：１と命名される、そのような配置により、四面体空洞を有する２つの面の間の八面体層内に位置する八面体空洞を有する面を画定することが可能になり、各四面体層内の１つの面を画定することが可能になる。各四面体は、八面体層と共有のイオンO^{2-}を有する。他の３つのイオンO^{2-}の各々は、同じ四面体層の別の四面体と共有される。

【００１９】従って、結晶単位格子は、各側面に４個の四面体空洞を有する６個の八面体空洞からなる。元素Ｓｉ、Ａｌ、ＯおよびＨからなるフィライトの場合には、そのような配置は、理想的な式$Si_8(Al_4\square_2)O_{20}(OH)_4$に一致する。四面体空洞は、ケイ素元素を含み、ジ八面体空洞は、アルミニウム元素を含むが、この場合、３つの八面体空洞における１つは、空（□）である。そのようなアセンブリーは、電気的に中性である。多くの場合、半単位格子が使用される。これは、式：

【化１】

$$Si_4(Al_{2\gamma}\square_{\gamma})O_{10}(OH)_2$$

を有する。

【００２０】モンモリロナイト型フィロシリケートの場合には、八面体アルミニウム元素は、２価の元素により一部置き換えられる。この置換は、組織に陰電荷を与える。これは、層間スペース内に位置する交換可能な補償カチオンの存在を必要とする。層間スペースの厚みは、補償カチオンの種類とその水和状態とに依存する。さらに、このスペースは、水、アミン、塩、アルコール、塩基等のような他の化学種を収容することが可能である。

【００２１】本発明によるフィロシリケートは、後述される特徴を有するモンモリロナイト型２：１ジ八面体フィロシリケートである。これらのフィロシリケートにおいて、柱は、層間スペース内に導入されて（柱は、SiO_2、Al_2O_3、TiO_2、ZrO_2およびV_2O_5から選ばれる）、少なくとも２．０×１

0^{-9} mの格子間距離d_{001}　を生じるようにする。

【0022】橋状化(bridging)前の出発モンモリロナイト型2：1ジ八面体フィロシリケートの（半単位格子に対する）一般化学式は、次の通りである：

【化2】

$$M^{m+}_{x/m}\,(Si_4\,(T_{(2-x)}\,Mg_x\ddot{y})\,O_{10}\,(OH)_{(2-y)}\,F_y)^{x-}$$

（式中、

・Tは、第IIIA族の元素からなる群から選ばれる元素（例えばB、Al、Ga）、および鉄、マンガン、クロム、チタン、バナジウムを表す。

【0023】・Mは、第IA族、第IIA 族および第VIII族の元素のカチオン、窒素を含む有機カチオン、アンモニウムカチオンおよび希土類カチオンからなる群から選ばれる少なくとも1つの補償カチオンである。モンモリロナイト型2：1ジ八面体フィロシリケートが、合成により得られる場合には、カチオンは、反応媒質より生じるか、あるいは少なくとも1つの交換方法により導入される。有利には、反応媒質より生じるカチオンは、アルカリ類（リチウムを除く）、アンモニウムカチオン（NH_4^+）、窒素を含む有機カチオン（アルキルアンモニウムおよびアリールアンモニウムを含む）、並びに燐を含む有機カチオン（アルキルホスホニウムおよびアリールホスホニウムを含む）からなる群から選ばれる。Mもまた後合成イオン交換によるか、あるいは場合によっては活性化された天然モンモリロナイト上でのイオン交換により、導入される補償カチオンであってよい。このカチオンMは、元素周期表の第IA族、第IIA 族および第VIII族の元素のカチオン、希土類のカチオン（原子番号57～71（71は含まれる）の元素のカチオン）、窒素を含む有機カチオン（アルキルアンモニウムおよびアリールアンモニウムを含む）、並びにアンモニウム・カチオンからなる群から選ばれる。

【0024】・mは、カチオンMの原子価である。

【0025】・xは、0より大きく2より小さい、好ましくは0．1～0．8の数である。

【0026】・yは、0～2の数である。フィロシリケートがフッ素を含む場合、yは0より大きい。

【0027】

【化3】

・$\ddot{y}$は、8面体空洞を表す。

天然状態で使用される2：1ジ八面体フィロシリケートは、好ましくは温度20～200℃、常圧～20バールの圧力で、例えばHNO_3　、HCl、H_2SO_4　、H_3PO_4　等を用いる、例えば酸処理により活性化される。

【0028】橋状化前の2：1ジ八面体フィロシリケートのX線回折図表は、次のスペクトル線の存在により特徴付けられる：

・（1．49±0．01）×10^{-10}　mのd_{060}を特徴付けるスペクトル線。

【0029】・d_{001}　が、補償カチオンの種類と検討される湿度でのその水和状態とに応じて（1．25±0．3）×10^{-9} mであるような少なくとも1つの反射001。

【0030】これらの2：1ジ八面体フィロシリケートは、例えば次の工程を含む方法により橋状化される：

・2：1ジ八面体フィロシリケートは、0．01～1モル／リットル、好ましくは0．05～0．7モル／リットルの範囲内の濃度を有する界面活性剤の溶液中に懸濁状にされる。この工程において使用可能な界面活性剤は、例えば限定されない例としてアルキル硫酸塩およびアルキルスルホン酸塩のようなアニオン性界面活性剤か、さもなければカチオン性界面活性剤である。カチオン性界面活性剤として、ハロゲン化または水酸化テトラアルキルアンモニウム、例えば塩化セチルトリメチルアンモニウムあるいはさらには双生のアルキルアンモニウム化合物が挙げられる。

【0031】例として、臭化ヘキサデシルトリメチルアンモニウム、臭化エチルヘキサデシルジメチルアンモニウム、臭化オクタデシルトリメチルアンモニウム、臭化ドデシルトリメチルアンモニウムおよび臭化ジドデシルジメチルアンモニウムが使用可能である。さらに中性界面活性剤、例えばトリトンX－100またはポリエチレンオキシド（POE）を使用してもよい。

【0032】媒質が、例えば5分～12時間、好ましくは15分～6時間、より好ましくは15分～3時間撹拌される接触時間の後に、全体は、沪過され、次いで蒸留水で洗浄され、次いで最後に空気または不活性ガス下に温度40～150℃で5分～24時間、好ましくは30分～12時間乾燥される。

【0033】フィロシリケートが、アンモニウム形態でない場合には、このフィロシリケートは、当業者に公知のあらゆる処理を予め受けて、主にアンモニウム形態の2：1ジ八面体フィロシリケートを得るようにする。この変換を行うための処理の限定されない例として、アンモニウム塩（硝酸アンモニウムおよび／または塩化アンモニウム）の水溶液によるイオン交換が挙げられる。

【0034】・次いで先行工程に記載された操作方法により処理された2：1ジ八面体フィロシリケートは、下記を含む混合物と接触させられる：

i)　少なくとも1つのRNH_2　型第1アミンまたはR'RNH型第2アミン（ここにおいて、RおよびR'は、有利には他の基により置換されるか、あるいは置換されない、炭素原子数1～16を有しうる炭素含有基、アルキル基、イソ・アルキル基、ナフテニル基および芳香族基からなる群から選ばれる）。

【0035】ii)　元素の少なくとも1つのアルコキシドまたはアルコキシドの混合物。元素は、ケイ素、アルミニウム、ジルコニウム、チタンおよびバナジウムからなる群から選ばれる。該アルコキシドは一般式M（O

R）n（式中、Mは、上記元素であり、nは、前記元素の原子価であり、Rは、有利には置換または非置換アルキル基、イソ・アルキル基、ナフテニル基および芳香族基からなる群から選ばれる基である）で示される。

【００３６】種々の基－ORは、上記で定義された群から選ばれるR基の種類に応じて同一または異なってよい。

【００３７】全体は、5分～１２時間、好ましくは5分～8時間、好ましくは撹拌下に接触放置される。

【００３８】iii） 次いで、こうして橋状化された２：１ジ八面体フィロシリケートは、沪過され、ついで空気下または不活性ガス下に温度４０～１５０℃で5分～２４時間、好ましくは３０分～１２時間乾燥される。

【００３９】慣行的には、乾燥後、フィロシリケートは、有利には温度を上昇させて焼成に付される。温度は、８００℃まで、好ましくは３００～８００℃、より有利には４００～８００℃に上昇されてよい。焼成時間は変動する。一般に温度は、１～１０時間、好ましくは４～8時間維持される。次いで固体を冷却させておく。

【００４０】この橋状化方法により、SiO_2、Al_2O_3、TiO_2、ZrO_2およびV_2O_5である柱、あるいはこれら柱の混合物を、２：１ジ八面体フィロシリケートの層間スペース内に簡単に迅速に導入することが可能になる。

【００４１】橋状化前の２：１ジ八面体フィロシリケートに関連して、本発明によるフィロシリケートは、X線回折のスペクトルを有する。従って、このスペクトルにより、少なくとも2.0×10^{-10} mの値に明らかに増大される格子間距離d_{001}を算定することが可能になる。さらに比表面積が、一般に２００～１０００m^2／g、好ましくは２５０～７００m^2／gに増大されるのが認められる。X線回折スペクトルの線d_{060}は、保持される。

【００４２】さらに本発明は、少なくとも2.0×10^{-9} mの格子間距離を有し、かつSiO_2、Al_2O_3、TiO_2、ZrO_2およびV_2O_5からなる群から選ばれる化合物のうちの少なくとも１つの化合物、あるいはこれらの化合物のあらゆる組み合わせをベースとする柱を含む（先に記載されたような）少なくとも１つのモンモリロナイト型２：１ジ八面体フィロシリケートと、少なくとも１つのマトリックスと、場合によってはゼオライトYとを含む触媒にも関する。好ましくは、該フィロシリケートは、少なくとも柱SiO_2を含むか、あるいはSiO_2と、Al_2O_3、TiO_2、ZrO_2およびV_2O_5からなる群から選ばれる化合物のうちの少なくとも１つの化合物との組み合わせをベースとする柱を含む。

【００４３】本発明の触媒もフォージャサイト構造型ゼオライトY（Zeolite Molecular Sieves Structure、Chemistry and Uses、D.W.BRECK 、J. WILLEY and Sons 1973年）、特に格子パラメータ（２４．２４～２４．５５）$\times10^{-10}$ mの脱アルミニウムゼオライトYを含んでよい。使用可能なゼオライトYのうち、好ましくは金属カチオン、例えばアルカリ土類金属カチオンおよび／または原子番号５７～７１（７１は含まれる）の希土類金属カチオンを用いて少なくとも一部交換される形態か、あるいは水素型形態の一般に超安定性ゼオライトすなわちＵＳＹと呼ばれる、安定化ゼオライトYが使用される。

【００４４】酸型ゼオライトH－Yは、特に有利でありかつ種々の規格により特徴付けられる：SiO_2／Al_2O_3モル比8～７０、好ましくは約１２～４０。１１００℃で焼成されるゼオライトについて測定される０．１５重量%未満のナトリウム含有量。元素状単位格子の格子パラメータ24.55×10^{-10} m～24.24×10^{-10} m、好ましくは24.38×10^{-10} m～24.26×10^{-10} m。改質され、中性化され、次いで焼成されたゼオライト１００グラム当たりNaのグラム数で表示される、約０．８５を越えるナトリウムイオンの取込み容量CNa。B．E．T．法により測定される約４００m^2／gを越える、好ましくは５５０m^2／gを越える比表面積。２．６トール（すなわち３４．６MPa）の分圧における温度２５℃での約6%を越える水蒸気吸着容量。直径20×10^{-10} m～80×10^{-10} mの細孔内に含まれるゼオライトの総細孔容積5～４５%、好ましくは5～４０%と、直径80×10^{-10} mを越えかつ一般に1000×10^{-10} m未満の細孔内に含まれるゼオライトの総細孔容積5～４５%、好ましくは5～４０%とを含み、また細孔容積の残部は、直径20×10^{-10} m未満の細孔内に含まれる、窒素の物理吸着により測定される細孔分布。

【００４５】さらに本発明の触媒は、通常例えばアルミナ、シリカ、酸化マグネシウム、酸化チタン、酸化ジルコニウム、燐酸アルミニウム、燐酸チタンまたは燐酸ジルコニウム、酸化ホウ素、これらの化合物のうちの少なくとも２つの化合物の組み合わせ、およびアルミナ・酸化ホウ素の組み合わせからなる群から選ばれる少なくとも１つの非晶質または不完全結晶化（低結晶度）マトリックスを含む。

【００４６】マトリックスは、好ましくはシリカ、アルミナ、酸化マグネシウム、シリカ・アルミナの組み合わせ、およびシリカ・酸化マグネシウムの組み合わせからなる群から選ばれる。

【００４７】従って本発明の触媒は、

ａ） 少なくとも１つの橋状２：１ジ八面体フィロシリケート１～８０%、あるいはさらには4～７０重量%、好ましくは１０～６０重量%、より好ましくは１５～５０重量%と、

ｂ） 好ましくは前述の特徴を有する少なくとも１つの

水素型フォージャサイト構造ゼオライトＹ　０（すなわち０．１）～３０重量%、好ましくは０（すなわち０．１）～２０重量%、より好ましくは０（すなわち０．１）～１０重量%と、

ｃ）　先に定義された少なくとも１つのマトリックス１～９９重量%とを含む。

【００４８】本発明の触媒は、当業者に公知のあらゆる方法により調製されてよい。本発明における好ましい方法のうちの１つは、湿潤アルミナゲル中において橋状２：１ジ八面体フィロシリケートと、場合によってはゼオライトＹとを数十分間混練させ、次いでこうして得られたペーストをダイに通して直径０．４～４ｍｍの押出し物を成形することからなる。次いで触媒は、好ましくは室温～２５０℃の温度で例えば乾燥炉での乾燥の後に、一般に温度約２５０～６００℃で焼成される。さらに一般に、該触媒は、例えば水素化・脱水素化機能を有する金属のような少なくとも１つの触媒元素を含む。一般に水素化・脱水素化機能は、例えば特にニッケルおよびコバルトのような第VIII族の少なくとも１つの金属または金属化合物により確保される。元素周期表の第VI族の少なくとも１つの金属（特にモリブデンまたはタングステン）あるいは金属化合物と、第VIII族の少なくとも１つの金属（特にコバルトまたはニッケル）あるいは金属化合物との組み合わせが使用されてよい。第VI族および／または第VIII族の金属酸化物の全体濃度は、１～４０重量%、好ましくは３～４０重量%、有利には８～４０重量%、より好ましくは１０～４０重量%、最も好ましくは１０～３０重量%である。第VIII族の金属（または複数金属）に対する第VI族の金属（または複数金属）の金属酸化物で表示される重量比は、１．２５～２０、好ましくは２～１０である。さらに、この触媒は、燐を含むものである。酸化燐P_2O_5の濃度で表示される燐含有量は、１５重量%未満、好ましくは１０重量%未満である。

【００４９】先に定義された水素化機能（第VIII族の金属、あるいは第VI族および第VIII族の金属の酸化物の組み合わせ）は、調製の種々のレベルにおいて種々の方法で触媒中に導入されてよい。

【００５０】該水素化機能は、一部のみ（第VI族および第VIII族の金属の酸化物の組み合わせの場合）、あるいは橋状２：１ジ八面体フィロシリケートと、マトリックスとして選ばれる酸化物ゲルとの混練時において全部導入されてよい。この水素化機能は、選ばれたマトリックス中に分散され、かつ場合によっては橋状である２：１ジ八面体フィロシリケートからなる焼成担体上での、選ばれた金属が第VIII族に属する場合には該金属の前駆体塩を含む溶液を用いて、１回または複数回のイオン交換操作により導入されてよい。この水素化機能は、第VI族の金属（特にモリブデンまたはタングステン）の酸化物の前駆体が、担体の混練時に予め導入されている場合、第VIII族の金属（特にコバルトおよびニッケル）の酸化物の前駆体溶液による、焼成されかつ成形された担体の１回または複数回の含浸操作により導入されてよい。最後に、この水素化機能は、第VI族および／または第VIII族の金属酸化物の前駆体を含む溶液による、橋状２：１ジ八面体フィロシリケートとマトリックスとからなる焼成担体の１回または複数回の含浸操作により導入されてよい。第VIII族金属の酸化物の前駆体は、好ましくは第VI族金属の酸化物の前駆体の後に、あるいはこれらの第VI族金属の酸化物の前駆体と同時に導入される。

【００５１】金属の酸化物が、対応する前駆体塩の複数の含浸工程において導入される場合には、触媒の中間焼成工程は、温度２５０～６００℃で行われねばならない。

【００５２】モリブデンの含浸は、パラモリブデン酸アンモニウム溶液中への燐酸の添加により促進されてよい。

【００５３】従って、得られた触媒は、一般に炭化水素の転換、特に水素化クラッキングにおいて使用される。これら触媒は、先行技術のゼオライト触媒に比して、水素化クラッキングにおいて非常に高品質の中間留分の製造に関して改善された選択性を示す。

【００５４】本方法において使用される仕込原料は、ガスオイル、減圧ガスオイル、脱アスファルト残渣または水素化処理済み残渣、あるいはそれらの同等物である。それらは、沸点３５０～５８０℃の化合物（すなわち炭素原子数少なくとも１５～２０を含む化合物に対応する）の少なくとも８０容積%からなる重質留分であってよい。これら重質留分は、一般に硫黄および窒素のようなヘテロ原子を含む。窒素含有量は、通常１～５０００重量ｐｐｍである。硫黄含有量は、０．０１～５重量%である。温度、圧力、水素の再循環割合および毎時空間速度のような水素化クラッキング条件は、仕込原料の種類、所望物質の品質および精油業者に利用される設備設置に応じて大幅に変化するものである。

【００５５】温度は、一般に２３０℃を越え、多くの場合３００～４８０℃、好ましくは４５０℃未満である。圧力は、２ＭＰａ以上、一般に３ＭＰａを越え、さらには１０ＭＰａである。水素の再循環割合は、仕込原料１リットル当たり水素最小限には１００リットル、　多くの場合水素２６０～３０００リットルである。毎時空間速度は、一般に０．２～１０h^{-1}である。

【００５６】

【発明の実施の形態】次の実施例は、本発明を例証するが、何らその範囲を限定するものではない。

［実施例１］

橋状モンモリロナイトＳｉ

Prolabo 社により供給され、かつＢＥＴ比表面積２５７m^2／ｇを有する天然活性化モンモリロナイトＫ１０　３ｇを、０．７５Ｍの塩化ヘキサデシルトリメチルア

ンモニウム（C_{16}TMA-Cl）42gと、蒸留水150mlとで構成される溶液中に懸濁化した。室温で2時間30分間の撹拌後、全体を沪過し、200mlの蒸留水で洗浄し、ついで60℃で8時間乾燥させた。次いで、この試料1gを、オクチルアミン（$C_8H_{17}NH_2$）1.12gと、テトラエチルオルトケイ酸エチルSi（OC_2H_5）$_4$ 7.54gとで構成される混合物中に懸濁化した。室温で30分間の撹拌後、全体を沪過し、ついで60℃で8時間直接乾燥させた。次いで物質を、空気下に500℃で4時間焼成した。焼成に相次ぐ重量損失は、29%であった。従って、格子間距離（周期性）d_{001} は、29.5×10^{-10} m（2.95nm）の値に到達した。該試料は、濃褐色の色合いを有した。さらに熱処理を空気下に650℃で4時間行って、有機物質の全体酸化を導いた。500～650℃での重量損失は、9%であった。物質のd_{001} は、32.0×10^{-10} m（3.20nm）であり、そのBET比表面積は、577m^2/gであった。格子間距離（周期性）は、空気下、750℃で4時間の焼成後において41.8×10^{-10} m（4.18nm）であった。

【0057】［実施例2］

橋状モンモリロナイトSi

Prolabo 社により供給され、かつBET比表面積257m^2/gを有する天然活性化モンモリロナイトK10 3gを、0.75Mの塩化ヘキサデシルトリメチルアンモニウム（C_{16}TMA-Cl）42gと、蒸留水150mlとで構成される溶液中に懸濁化した。室温での2時間30分間の撹拌後、全体を沪過し、200mlの蒸留水で洗浄し、ついで60℃で8時間乾燥させた。次いで、この試料1gを、オクチルアミン（$C_8H_{17}NH_2$）0.56gと、テトラエチルオルトケイ酸エチルSi（OC_2H_5）$_4$ 7.54gとで構成される混合物中に懸濁化した。室温での30分間の撹拌後、全体を沪過し、ついで60℃で8時間直接乾燥させた。次いで物質を、空気下に500℃で4時間焼成した。焼成に相次ぐ重量損失は、25%であった。従って、格子間距離（周期性）d_{001} は、37.8×10^{-10} m（3.78nm）の値に到達した。さらに熱処理を空気下に650℃で4時間行った。500～650℃での重量損失は、6%であった。物質のd_{001} は、45.8×10^{-10} m（4.58nm）であり、そのBET比表面積は、500m^2/gであった。

【0058】［実施例3］

橋状モンモリロナイトSi

Prolabo 社により供給され、かつBET比表面積257m^2/gを有する天然活性化モンモリロナイトK10 3gを、0.75Mの塩化ヘキサデシルトリメチルアンモニウム（C_{16}TMA-Cl）42gと、蒸留水150mlとで構成される溶液中に懸濁化した。室温で2時間30分間の撹拌後、全体を沪過し、200mlの蒸留水で洗浄し、ついで60℃で8時間乾燥させた。次いで、この試料1gを、オクチルアミン（$C_8H_{17}NH_2$）1.12gと、テトラエチルオルトケイ酸エチルSi（OC_2H_5）$_4$ 15.08gとで構成される混合物中に懸濁化した。室温で30分間の撹拌後、全体を沪過し、ついで60℃で8時間直接乾燥させた。次いで物質を、空気下に500℃で4時間焼成した。焼成に相次ぐ重量損失は、22%であった。従って、格子間距離（周期性）d_{001} は、27.7×10^{-10} m（2.77nm）の値に到達した。さらに処理を、空気下に650℃で4時間行った。500～650℃での重量損失は、8.7%であった。物質のd_{001} は、30.4×10^{-10} m（3.04nm）であった。

【0059】［実施例4］

橋状モンモリロナイトSi

Prolabo 社により供給され、かつBET比表面積257m^2/gを有する天然活性化モンモリロナイトK10 3gを、0.75Mの塩化ヘキサデシルトリメチルアンモニウム（C_{16}TMA-Cl）21gと、蒸留水75mlとで構成される溶液中に懸濁化した。室温での2時間30分間の撹拌後、全体を沪過し、200mlの蒸留水で洗浄し、ついで60℃で8時間乾燥させた。次いで、この試料1gを、オクチルアミン（$C_8H_{17}NH_2$）0.56gと、テトラエチルオルトケイ酸エチルSi（OC_2H_5）$_4$ 7.54gとで構成される混合物中に懸濁化した。室温での30分間の撹拌後、全体を沪過し、ついで60℃で8時間直接乾燥させた。次いで物質を、空気下に500℃で4時間焼成した。焼成に相次ぐ重量損失は、24%であった。従って、格子間距離（周期性）d_{001} は、41.3×10^{-10} m（4.13nm）の値に到達した。さらに熱処理を、空気下に650℃で4時間行った。500～650℃での重量損失は、8%であった。物質のd_{001} は、42.0×10^{-10} m（4.20nm）であり、そのBET比表面積は、518m^2/gであった。

【0060】［実施例5］

橋状モンモリロナイトSi

Prolabo 社により供給され、かつBET比表面積257m^2/gを有する天然活性化モンモリロナイトK10 3gを、0.75Mの塩化ヘキサデシルトリメチルアンモニウム（C_{16}TMA-Cl）42gの溶液中に懸濁化した。室温での2時間30分間の撹拌後、全体を沪過し、200mlの蒸留水で洗浄し、ついで60℃で8時間乾燥させた。次いで、この試料1gを、オクチルアミン（$C_8H_{17}NH_2$）1.12gと、テトラエチルオルトケイ酸エチルSi（OC_2H_5）$_4$

7．54gとで構成される混合物中に懸濁化した。室温での30分間の撹拌後、全体を沪過し、ついで60℃で8時間直接乾燥させた。次いで物質を、空気下に500℃で4時間焼成した。焼成に相次ぐ重量損失は、29%であった。従って、格子間距離（周期性）d_{001}は、46．8×10^{-10} m（4．68nm）の値に到達した。さらに熱処理を、空気下に650℃で4時間行った。500～650℃での重量損失は、8%であった。物質のd_{001}は、40．1×10^{-10} m（4．01nm）であり、そのBET比表面積は、543m^2 ／gであった。後に行われるこの試料の750℃での焼成により、37．2×10^{-10} m（3．72nm）のd_{001}を有する物質が生じた。

【0061】［実施例6］

橋状モンモリロナイトSi

Prolabo 社により供給され、かつBET比表面積13m^2 ／gを有する天然活性化モンモリロナイトKSF 1．5gを、0．75Mの塩化ヘキサデシルトリメチルアンモニウム（C_{16}TMA－Cl）21gと、蒸留水75mlとで構成される溶液中に懸濁化した。室温での2時間30分間の撹拌後、全体を沪過し、200mlの蒸留水で洗浄し、ついで60℃で8時間乾燥させた。次いで、この試料1gを、オクチルアミン（$C_8H_{17}NH_2$） 0．56gと、テトラエチルオルトケイ酸エチルSi（OC_2H_5）$_4$ 7．54gとで構成される混合物中に懸濁化した。室温での30分間の撹拌後、全体を沪過し、ついで60℃で8時間直接乾燥させた。次いで物質を、空気下に500℃で4時間焼成した。焼成に相次ぐ重量損失は、24%であった。この場合、格子間距離（周期性）d_{001}は、37．2×10^{-10} m（3．72nm）の値に到達した。さらに熱処理を、空気下に650℃で4時間行った。500～650℃での重量損失は、6%であった。物質のd_{001}は、36．9×10^{-10} m（3．69nm）であり、そのBET比表面積は、506m^2 ／gであった。

【0062】［実施例7］

橋状モンモリロナイトSi／Zr

Prolabo 社により供給され、かつBET比表面積257m^2 ／gを有する天然活性化モンモリロナイトK10 15gを、0．75Mの塩化ヘキサデシルトリメチルアンモニウム（C_{16}TMA－Cl）210gと、蒸留水75mlとで構成される溶液中に懸濁化した。室温での2時間30分間の撹拌後、全体を沪過し、200mlの蒸留水で洗浄し、ついで60℃で8時間乾燥させた。次いで、この試料2gを、オクチルアミン（$C_8H_{17}NH_2$） 1．12gと、テトラエチルオルトケイ酸エチルSi（OC_2H_5）$_4$ 15．08gと、イソプロポキシドジルコニウムZr（OC_3H_7） 0．59gとで構成される混合物中に懸濁化した。室温での30分間の撹拌後、全体を沪過し、ついで60℃で8時間直接乾燥させた。次いで物質を、空気下に650℃で4時間焼成した。焼成に相次ぐ重量損失は、26%であった。従って、格子間距離（周期性）d_{001}は、43．6×10^{-10} m（4．36nm）の値に到達した。BET比表面積は、510m^2 ／gであった。

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(54) MONTMORILLONITE TYPE BRIDGED 2:1 DIOCTAHEDRAL PHYLLOSILICATE HAVING LARGE DISTANCE BETWEEN LATTICES, CATALYST AND CONVERTING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a montmorillonite type 2:1 dioctahedral phyllosilicate, which is an activated natural material or obtained by synthesis.
SOLUTION: Montmorillonite type 2:1 dioctahedral phyllosilicate has at least 2.00×10-9 m interplanar spacing and contains at least one of compounds selected from a group composed of SiO2, Al2O3, TiO2, ZrO2 and V2O5 or a pillar composed of the combination of the compounds as the base in the interlaminar space.

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CLAIMS

[Claim(s)]

[Claim 1] the distance between [of at least 2.00x10 to 9 m] grids -- having -- and SiO2 aluminum2 O3 TiO2 ZrO2 And V2 O5 from -- montmorillonite type 2:1 JI octahedron phyllosilicate which contains the pillar which uses all combination of at least one compound in the compound chosen from the becoming group, or these compounds as the base in the space between layers

[Claim 2] 2:1 JI octahedron phyllosilicate containing a fluorine according to claim 1.

[Claim 3] 2:1 JI octahedron phyllosilicate according to claim 1 or 2 whose distance between grids is at least 2.65x10 to 9 m.

[Claim 4] 2:1 JI octahedron phyllosilicate given [of the claims 1-3 whose distance between grids is at least 3.0x10 to 9 m] in any 1 term.

[Claim 5] 2:1 JI octahedron phyllosilicate given [of the claims 1-4 whose distance between grids is at least 3.3x10 to 9 m] in any 1 term.

[Claim 6] 2:1 JI octahedron phyllosilicate given [of the claims 1-5 whose distance between grids is at most 6.0x10 to 9 m] in any 1 term.

[Claim 7] Pillar SiO2 2:1 JI octahedron phyllosilicate given [of the included claims 1-6] in any 1 term.

[Claim 8] SiO2 aluminum2 O3 TiO2 ZrO2 And V2 O5 from -- 2:1 JI octahedron phyllosilicate given [of the claims 1-7 containing the pillar which makes **-SU combination with at least one compound in the compound chosen from the becoming group] in any 1 term

[Claim 9] The manufacture method of the 2:1 JI octahedron phyllosilicate which is contacted with mixture and which has the distance between of at least 2.00x10 to 9 m] grids characterized by providing the following. After slurrying of the phyllosilicate is carried out into the solution of a surfactant and it subsequently separates a solid-state from a solution, phyllosilicate is the 1st or 2nd at least one amine. At least one alkoxide of the element chosen from the group which consists of Si, aluminum, Zr, Ti, and V.

[Claim 10] The way according to claim 9 the phyllosilicate made into the letter of suspension is an ammonium (NH4+) type.

[Claim 11] The way according to claim 9 or 10 the solution of a surfactant has the concentration of 0.01-1 mol/l.

[Claim 12] primary amine RNH2 the [or] -- 2 amine R'RNH -- an alkyl -- It has the R group and R' machine of the carbon atomic numbers 1-16 which are chosen from the group which consists of an ISO alkyl, NAFUTENIRU and substitution, or unsubstituted aromatic machine. Moreover, the method of given [of the claims 9-11, in which alkoxide M(OR) n of Element M has the R group of the carbon atomic numbers 1-16 chosen from the group which consists of an alkyl, ISO alkyl NAFUTENIRU and substitution, or unsubstituted aromatic machine] in any 1 term.

[Claim 13] The catalyst which contains Zeolite Y depending on the case with at least one 2:1 JI octahedron phyllosilicate prepared by the any 1 term publication of the any 1 term publication of the claims 1-8, or the claims 9-12, and at least one matrix.

[Claim 14] The catalyst which contains Zeolite Y depending on the case with at least one 2:1 JI octahedron phyllosilicate prepared by the any 1 term publication of the claims 9-12, and at least one matrix.

[Claim 15] - at least one 2:1 JI octahedron phyllosilicate 1 - 80 % of the weight, and - at least one zeolite Y 0 - 30 % of the weight, and - at least one matrix Catalyst containing 1 - 99 % of the weight according to claim 13 or 14.

[Claim 16] A catalyst given [of the claims 13-15 which furthermore contain at least one catalyst element] in any 1 term.

[Claim 17] The catalyst according to claim 16 whose catalyst elements are hydrogenation and a dehydrogenation element.

[Claim 18] A catalyst given [of the claims 13-17 which furthermore contain phosphorus] in any 1 term.

[Claim 19] A catalyst given [of the claims 13-18 chosen from the group which a matrix becomes from an alumina, a silica, a magnesium oxide, titanium oxide, a zirconium oxide, phosphoric acid titanium, a zirconium phosphate, and boron oxide] in any 1 term.

[Claim 20] A catalyst given [of the claims 13-19 containing the 2:1 JI octahedron phyllosilicate containing a fluorine] in any 1 term.

[Claim 21] A catalyst given [of the claims 13-20 containing the dealuminization zeolite Y] in any 1 term.

[Claim 22] The hydrocarbon conversion method using a catalyst given [of the claims 13-21] in any 1 term.

[Claim 23] The method according to claim 22 in hydrogenation cracking using the catalyst which furthermore contains at least one hydrogenation and a dehydrogenation element.

[Claim 24] the temperature of 230 degrees C or more, and a pressure -- the method according to claim 23 of operating it by 2MPa(s) and VVH0.2-10h-1, even if few

[Claim 25] The method according to claim 23 or 24 of operating it about a gas oil, a reduced pressure gas oil, a deasphalting residue, or a hydrogen-treating finishing residue.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention is the nature activated, for example, or relates to the montmorillonite type 2:1 JI octahedron phyllosilicate obtained by composition. The aforementioned composition is performed into a fluoride medium to the bottom of existence of a hydrofluoric acid and/or another source of a fluoride anion depending on the case. the aforementioned phyllosilicate -- the shape (bridged) of a bridge it is -- and big distance between grids (interplanar spacing) It has. d001 The distance between grids expressed is the sum total of the thickness of a layer (sheet), and the space between layers.
[0002] Furthermore, this invention relates also to the manufacture method for obtaining the aforementioned phyllosilicate.
[0003] These phyllosilicate may be contained in the constituent of the catalyst used in hydrogenation cracking of a hydrocarbon brewing raw material.
[0004] further -- this invention -- for example, the activated nature -- namely, -- for example, or it was processed from the acid, depending on the case, it is compounded in a fluoride medium (under existence of a hydrofluoric acid and/or another source of a fluoride anion), and is related also with the catalyst containing at least one montmorillonite type 2:1 JI octahedron phyllosilicate [-izing / the shape of a bridge / subsequently / phyllosilicate] The aforementioned phyllosilicate has a big distance between grids (the distance between this grid is the sum total of the thickness of a layer (sheet sheet), and the space between layers (space between the sheets)). Furthermore, a catalyst contains at least one faujasite structured type zeolite Y with at least one matrix depending on the case. Furthermore, this invention relates also to the conversion method of a hydrocarbon brewing raw material of using this catalyst, especially the hydrogenation cracking method.
[0005]
[Description of the Prior Art] Hydrogenation cracking of a heavy petroleum fraction is the very important method of petroleum refining, and it becomes possible to manufacture a light fraction like a gasoline, evaporation fuel, and a light gas oil by this refining method from the heavy brewing raw material of the surplus which does not almost have added value. A refiner searches for these light fractions in order to fit the manufacture to the need of a commercial scene. It is that the merit of catalytic hydrogenation cracking supplies a very quality middle cut, evaporation fuel (jet fuel), and a gas oil as compared with contact cracking. On the other hand, the generated gasoline has a low octane value considerably rather than the gasoline produced according to contact cracking.
[0006] The catalysts used in hydrogenation cracking are all dual-function [which combines an acid function and a hydrogenation function] type catalysts. An acid function is brought about with the combination of support, for example, a halogenation (especially chlorination or fluoridation) alumina, boron oxide, and aluminum, amorphous-silica alumina, and zeolite of a big specific surface area (generally 150-800m2 /g) which has surface acidity. a hydrogenation function -- the [element periodic-table] -- or it is based on one or more metal, for example, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmiums, iridium, and platinum of a VIII group -- the [or / element periodic-table] -- the [at least one metal of VI group, for example, chromium, molybdenum and a tungsten, and] -- it is brought with combination with at least one metal of a VIII group
[0007] The balance between the dual functions which are an acid function and a hydrogenation function is a fundamental parameter. The activity and selectivity of a catalyst are determined with this parameter. By the weak-acid function and the strong hydrogenation function, the catalyst which is hardly activity (the degree of subvital) is offered. These are equipped with the very high selectivity of a middle cut although these catalysts generally act at an elevated temperature (390 degrees C or more) with a low space speed of supply (VVH displayed to the capacity of the brewing raw material which should be processed per one unit of catalyst capacity is generally two or less per hour). On the contrary, although a very activity catalyst is offered by the strong acid function and the weak hydrogenation function, these show low selectivity in a middle cut. Therefore, it is possible by choosing each of these functions appropriately to adjust the lot of the activity/selectivity of a catalyst.
[0008] Therefore, it is one of the big merits of hydrogenation cracking to have big adaptability (flexibility) (flexibility), i.e., the adaptability about the catalyst used, in some level. The adaptability (flexibility) of the brewing raw material which should be processed about the obtained matter with this adaptability (flexibility) is brought about. The parameter with easy controlling is the acidity of a catalyst support.
[0009] The conventional catalytic hydrogenation cracking catalyst consists of support which is acescence, for example, an amorphous-silica alumina, in the most. In order to manufacture a very quality middle cut, these systems are further used, in order that the acidity may manufacture stock oil to a low case very much.
[0010] An amorphous-silica alumina is acescence support. the hydrogenation cracking catalyst of a large number in a commercial scene -- the -- the case where the content of the hetero atom poison (for example, S, N, and a heavy metal) of the silica alumina combined with a VIII group's metal or the brewing raw material which should be processed exceeds 0.5 % of the weight preferably -- the -- VIB the [a group and] -- it consists of silica aluminas combined with the combination of the sulfide a VIII group's metal These systems have the very high selectivity of a middle cut. The generated matter has high quality. Furthermore, it is also most possible among those catalysts for such a catalyst to manufacture lubricous stock oil about the thing of the acescence. It is the weak activity un-arranging [of all these catalyst systems that use amorphous support as the base], as mentioned already.
[0011]
[Elements of the Invention] A bird clapper came [by the research achievements performed by these people, / although it was not expecting / in the catalyst containing at least one montmorillonite type 2:1 JI octahedron phyllosilicate / improving the performance in hydrogenation cracking

as compared with the well-known catalyst in the advanced technology] to be proved possible. Depending on the natural phyllosilicate activated namely, processed from the acid, or the case, this JI octahedron phyllosilicate is compounded in a fluoride medium (under existence of hydrofluoric-acid HF and/or another source of a fluoride anion), subsequently are-izing [phyllosilicate / the shape of a bridge] (method preferably indicated by this specification), and it is combined with the zeolite Y of a faujasite structured type depending on the case.
[0012] In accuracy, this invention is d001 of at least 2.0x10 to 9 m more. . the distance between grids expressed -- having -- and SiO2 aluminum2 O3 TiO2 ZrO2 And V2 O5 from -- it is related with the montmorillonite type 2:1 JI octahedron phyllosilicate which contains the pillar (pillar) which uses all combination of at least one compound in the compound chosen from the becoming group, or these compounds as the base in the space between layers desirable -- phyllosilicate -- pillar SiO2 or it contains -- otherwise, SiO2 aluminum2 O3 TiO2 ZrO2 And V2O5 from -- the pillar which uses combination with at least one compound in the compound chosen from the becoming group as the base is included Depending on the case, this phyllosilicate contains a fluorine.
[0013] According to this invention (put under existence of hydrofluoric-acid HF and/or another source of a fluoride anion in a fluoride medium depending on the case.) These bridge-like 2:1 JI octahedron phyllosilicate prepared beforehand is the distance d001 between grids which exceeds 2.8x10 to 9 m more preferably, or exceeds further 3.0x10 to 9 m at least 2.65x10 to 9 m preferably at least 2.0x10 to 9 m. It has. Especially the distance of at least 3.3x10 to 9 m is a pillar SiO2. Or pillar SiO2 It obtains and gets in an oxide besides +. Generally 6.0x10 - 9 or less m of distance between this grid is 5.0x10 - 9 or less m preferably. d001 The distance between grids displayed expresses the sum total of the thickness of a layer (sheet), and the space between layers. Using the conventional powder X-ray diffractometry (orientated) by which orientation was carried out, this value is acquired directly and it deals in it.
[0014] Furthermore, this invention relates to the manufacture method of the aforementioned phyllosilicate. In this method, after making phyllosilicate into the letter of suspension into the solution of a surfactant and separating a solid-state from this solution subsequently, this phyllosilicate is contacted with the mixture containing the 1st or 2nd at least one amine and at least one alkoxide of the element chosen from the group which consists of Si, aluminum, Zr, Ti, and V. Preferably, at least one silicon alkoxide is used with at least one alkoxide of the element chosen from the group which consists of aluminum, Zr, Ti, and V depending on the case.
[0015] 2:1 JI octahedron phyllosilicate is a mineral produced by the pile of an element-like layer (sheet). Although the chemical bond between the elements of phyllosilicate structure is ion covalent bond, it is assumed that these chemical bonds are ionicity in order to make this specification simple.
[0016] It is possible to acquire the field which has the hexagon-like cavity (cavity) called hexagon-like side by removing one ion O2- from two arrays of ion O2- from the display which ion O2- touches mutually in a flat surface.
[0017] The structure of FIRAITO is the hexagon-like side of ion O2-, and ion O2- and ion OH-. It is briefly expressed by arrangement with a compact side, and gets by it. The cavity of the hexagon-like side of ion O2- is filled by ion OH-. By the superposition of two compact sides into which both sides were inserted by the hexagon-like side, between two tetrahedral layers (T), it becomes possible to demarcate an octahedral layer (O), and naming of Layer (sheet) TOT originates from this.
[0018] It becomes possible to demarcate the field which has the octahedron cavity located in the octahedral layer between two fields which have a tetrahedron cavity, and such arrangement similarly named 2:1 enables it to demarcate one field in a fourth page each body whorl. Four face pieces each have an octahedral layer and shared ion O2-. Other three each of ion O2- is shared with another tetrahedron of the same tetrahedral layer.
[0019] Therefore, a crystal unit lattice becomes each side from six octahedron cavities which have four tetrahedron cavities. It is the formula Si 8 with such arrangement ideal in FIRAITO which consists of elements Si, aluminum, O, and H. (aluminum4 **2) O20 (OH) 4 It is in agreement. Although a tetrahedron cavity contains an aluminum element including a silicon element in a JI octahedron cavity, one [in / three octahedron cavities / in this case] is empty (**). Such an assembly is electrically neutral. In many cases, a half-unit lattice is used. This is formula:.
[Formula 1] $Si_4(Al_{2}\ddot{y})O_{10}(OH)_2$

It ****.
[0020] In the case of montmorillonite type phyllosilicate, an octahedron aluminum element is replaced in part with a divalent element. This substitution gives an organization negative charge. This needs existence of the exchangeable compensation cation located in the space between layers. It depends for the thickness of the space between layers on the kind and its hydration state of a compensation cation. Furthermore, this space can hold other chemical species, such as water, an amine, a salt, alcohol, and a base.
[0021] The phyllosilicate by this invention is montmorillonite type 2:1 JI octahedron phyllosilicate which has the feature mentioned later. In these phyllosilicate, a pillar is introduced in the space between layers (a pillar is chosen from SiO2 , aluminum2 O3 , TiO2 , ZrO2 , and V2 O5), and it is the distance d001 between [of at least 2.0x10 to 9 m] grids. It is made to be generated.
[0022] The general (as opposed to half-unit lattice) chemical formula of the start montmorillonite type 2:1 JI octahedron phyllosilicate before shape[of a bridge]-izing (bridging) is : which is as follows. [Formula 2]
$M^{m+}_{x/m}(Si_4(T_{(2-x)}Mg_x\ddot{y})O_{10}(OH)_{(2-y)}F_y)^*$

inside of formula, and -T -- the -- the element (for example, B, aluminum, Ga) chosen from the group which consists of an IIIA group's element and iron, manganese, chromium, titanium, and vanadium are expressed
[0023] - M -- the -- the [IA group and] -- IIA the [a group and] -- it is at least one compensation cation chosen from the group which consists of the cation of a VIII group's element, the organic cation containing nitrogen, an ammonium cation, and a rare earth cation When montmorillonite type 2:1 JI octahedron phyllosilicate is obtained by composition, it is generated from a reaction medium or a cation is introduced by at least one exchange method. Advantageously, the cation produced from a reaction medium is chosen from the group which consists of alkali (except for a lithium), an ammonium cation (NH4+), an organic cation (alkylammonium and aryl ammonium are included) containing nitrogen, and an organic cation (an alkyl phosphonium and an aryl phosphonium are included) containing phosphorus. You may be the compensation cation introduced by the ion exchange on the natural montmorillonite which also depended M on the post-composition ion exchange, or was activated depending on the case. this cation M -- the [of an element periodic table] -- the [IA group and] -- IIA the [a group and] -- it is chosen out of the group which consists of the cation of a VIII group's element, the cation (cation of the element of the atomic numbers 57-71 (71 is contained)) of rare earth, an organic cation (alkylammonium and aryl ammonium are included) containing nitrogen, and an ammonium cation
[0024] - m is the valence of Cation M.

[0025] - x is more greatly [than 0] smaller than 2 -- it is the number of 0.1-0.8 preferably
[0026] - y is the number of 0-2. When phyllosilicate contains a fluorine, y is larger than 0.
[0027]
[Formula 3]
• ☐は、8面体空洞を表す。

the 2:1 JI octahedron phyllosilicate used in the state of nature -- desirable -- the temperature of 20-200 degrees C, and an ordinary-pressure -20 bar pressure -- it is -- for example, HNO3 HCl and H2SO4 H3 PO4 etc. -- acid treatment is used for example, activated
[0028] The X diffraction chart of the 2:1 JI octahedron phyllosilicate before shape[of a bridge]-izing is : and (1.49**0.01) x10-10 characterized by existence of the following spectral line. d060 of m The characterized spectral line.
[0029] - d001 At least one reflection 001 which is x(1.25**0.3)10-9m according to the kind of compensation cation, and its hydration state in the humidity examined.
[0030] : and 2:1 JI octahedron phyllosilicate are made into the letter of suspension into the solution of the surfactant which has preferably 0.01-1 mol /of concentration within the limits of 0.05-0.7 mols/l. l. [-izing / the shape of a bridge / with the way these 2:1 JI octahedron phyllosilicate includes the following process / phyllosilicate] If there is no usable surfactant as if in this process in an anionic surfactant like an alkyl sulfate and an alkyl sulfonate as an example which is not limited, for example, it is a cation nature surfactant. As for halogenation, a tetraalkylammonium hydroxide, for example, chlorination cetyl trimethylammonium, or a further, the alkylammonium compound of the gemination is mentioned as a cation nature surfactant.
[0031] as an example -- bromination -- hexadecyl trimethylammonium, ethyl-bromide hexadecyl dimethylannmonium, and bromination -- octadecyl trimethylammonium, a dodecyltrimethylammonium bromide, and bromination -- didodecyl dimethylannmonium is usable Furthermore, you may use the neutral surfactant X-100, for example, a triton, or a polyethylene oxide (POE).
[0032] As for the whole, a medium is filtered after 5 minutes - 12 hours and the contact time agitated more preferably for 15 minutes to 3 hours for 15 minutes to 6 hours, and subsequently it is washed by distilled water, and, subsequently to the bottom of air or inert gas, finally, dries preferably at the temperature of 40-150 degrees C for 30 minutes to 12 hours for 5 minutes to 24 hours.
[0033] When phyllosilicate is not an ammonium gestalt, this phyllosilicate mainly obtains the 2:1 JI octahedron phyllosilicate of an ammonium gestalt to this contractor, beforehand in response to the fact that all well-known processings. As an example to which the processing for performing this conversion is not limited, the ion exchange by the solution of an ammonium salt (an ammonium nitrate and/or ammonium chloride) is mentioned.
[0034] - 2:1 JI octahedron phyllosilicate processed by the operating instruction subsequently to a precedence process indicated, :i contacted into the mixture containing the following At least one RNH2 Type primary amine, or the R'RNH type 2nd amine (in here, R and R' is chosen from the group which consists of the carbon content machine which may have the carbon atomic numbers 1-16 which are advantageously replaced by other bases or are not replaced, an alkyl group, an isoalkyl group, a NAFUTENIRU machine, and an aromatic machine).
[0035] ii) Mixture of at least one alkoxide of an element, or an alkoxide. An element is chosen from the group which consists of silicon, aluminum, a zirconium, titanium, and vanadium. This alkoxide is shown by general formula M(OR) n (M is the above-mentioned element among a formula, n is the valence of the aforementioned element, and R is a basis advantageously chosen from the group which consists of substitution or an unsubstituted alkyl group, an isoalkyl group, a NAFUTENIRU machine, and an aromatic machine).
[0036] various basis-OR is the same according to the kind of R group chosen from the group defined above -- or you may differ
[0037] Contact neglect of the whole is preferably carried out under churning for 5 minutes to 8 hours for 5 minutes to 12 hours.
[0038] iii Subsequently, the 2:1 JI octahedron phyllosilicate [-izing / the shape of a bridge / in this way / phyllosilicate] is filtered, and, subsequently to the bottom of air or inert gas, is preferably dried at the temperature of 40-150 degrees C for 30 minutes to 12 hours for 5 minutes to 24 hours.
[0039] Habitually, after dryness, advantageously, phyllosilicate raises temperature and is given to baking. Temperature may rise at 400-800 degrees C more advantageously by 300-800 degrees C preferably to 800 degrees C. A firing time is changed. Generally temperature is maintained preferably for 4 to 8 hours for 1 to 10 hours. Subsequently, the solid-state is made to cool.
[0040] this shape-ized method of a bridge -- SiO2 aluminum2 O3 TiO2 ZrO2 and V2 O5 it is -- it becomes possible to introduce the mixture of a pillar or these pillars quickly simply in the space between layers of 2:1 JI octahedron phyllosilicate
[0041] In relation to the 2:1 JI octahedron phyllosilicate before shape[of a bridge]-izing, the phyllosilicate by this invention has the spectrum of an X diffraction. Therefore, it is at least 2.0x10-10 by this spectrum. Distance d001 between grids which increases to the value of m clearly It becomes possible to calculate. further -- specific surface area -- general -- 200-1000m2 /g -- desirable -- 250-700m2 Increasing to /g is admitted. Line d060 of an X diffraction spectrum It is held.
[0042] Furthermore, this invention has the distance between [of at least 2.0x10 to 9 m] grids. and SiO2 aluminum2 O3 TiO2 ZrO2 And V2 O5 from -- at least one compound in the compound chosen from the becoming group -- Or depending on the case, it is related also with the catalyst which contains Zeolite Y with at least one montmorillonite type 2:1 JI octahedron phyllosilicate containing the pillar (as [indicated / previously]) which uses all combination of these compounds as the base, and at least one matrix. desirable -- this phyllosilicate -- at least -- pillar SiO2 or it contains -- or SiO2 aluminum2 O3 TiO2 ZrO2 And V2 O5 from -- the pillar which uses combination with at least one compound in the compound chosen from the becoming group as the base is included
[0043] the catalyst of this invention -- the faujasite structured type zeolite Y (Zeolite Molecular Sieves Structure, Chemistry and Uses, D.W.BRECK, J.WILLEY and Sons 1973) -- especially -- lattice-parameter (24.24-24.55) x10-10 The dealuminization zeolite Y of m may be included. The stabilization zeolite Y generally [the gestalt preferably exchanged in part at least among the usable zeolites Y using a metal cation, for example, an alkaline-earth-metal cation, and/or the rare-earth-metal cation of the atomic numbers 57-71 (71 is contained) or a hydrogen type gestalt] called hyperstability zeolite, i.e., USY, is used.
[0044] :SiO2 characterized by the various specification that acid type zeolite H-Y is especially advantageous and /aluminum2 O3 mole ratios 8-70 -- desirable -- about 12-40 Less than 0.15% of the weight of the sodium content measured about the zeolite calcinated at 1100 degrees C. lattice parameter 24.55x10-10 of an element-like unit lattice m to 24.24x10-10 m -- desirable -- 24.38x10-10 m to 24.26x10-10 m. Incorporation capacity CNa of the sodium ion exceeding about 0.85 which is reformed, and it is carbonated and is displayed with the number of grams of Na per [which was subsequently calcinated] 100g of zeolites. B.E.T. about 400 measured by law -- m2 /g is exceeded -- desirable --

550m2 Specific surface area exceeding /g. Steam adsorption capacity exceeding about 6% with a temperature [in the partial pressure of 2.6 torrs (namely, 34.6MPa(s))] of 25 degrees C. Diameter 20x10-10 m to 80x10-10 It is with 5 - 40% preferably the 5 - 45% of the total pore volume of the zeolite contained in the pore of m. Diameter 80x10-10 Generally [exceed m and] it is 1000x10-10. The 5 - 45% of the total pore volume of the zeolite contained in the pore of under m, 5 - 40% is included preferably, and the remainder of pore volume is a diameter 20x10-10. Pore distribution which is included in the pore of under m and which is measured by physical adsorption of nitrogen.

[0045] Furthermore, the catalyst of this invention includes at least one amorphous substance or imperfect-crystal-ized (low crystallinity) matrix chosen from the group which usually consists of an alumina, a silica, a magnesium oxide, titanium oxide, a zirconium oxide, an aluminum phosphate, phosphoric acid titanium or a zirconium phosphate, boron oxide, combination of at least two compounds in these compounds, and combination of an alumina and boron oxide, for example.

[0046] A matrix is chosen from the group which consists of combination of a silica, an alumina, a magnesium oxide, and a silica alumina, and combination of a silica and a magnesium oxide preferably.

[0047] Therefore, the catalyst of this invention is a. 1 - 80% of at least one bridge-like 2:1 JI octahedron phyllosilicate and a further are 15 - 50 % of the weight more preferably ten to 60% of the weight four to 70% of the weight. b) It is at least one hydrogen type faujasite structure zeolite Y which has the desirable above-mentioned feature. It is [0 (namely, 0.1) - 10 % of the weight, and] c more preferably zero (namely, 0.1) to 20% of the weight zero (namely, 0.1) to 30% of the weight. At least one matrix defined previously 1 - 99 % of the weight is included.

[0048] The catalyst of this invention may be prepared by this contractor by all well-known methods. One of the desirable methods in this invention consists of fabricating an extrusion object with a diameter of 0.4-4mm through the paste which Zeolite Y was made to knead for dozens of minutes with bridge-like 2:1 JI octahedron phyllosilicate in a humid alumina gel, and was subsequently obtained in this way in to a die depending on the case. Subsequently, preferably, with room temperature -250 degree C temperature, generally a catalyst is calcinated at the temperature of about 250-600 degrees C, after drying with a drying furnace. Furthermore, generally, this catalyst contains at least one catalyst element like the metal which has for example, hydrogenation and a dehydrogenation function. general -- hydrogenation and a dehydrogenation function -- the [for example, / like especially nickel and cobalt] -- it is secured with a VIII group's at least one metal or metallic compounds the [of an element periodic table] -- the [at least one metal (especially molybdenum or a tungsten) of VI group or metallic compounds, and] -- combination with at least one metal (especially cobalt or nickel) of a VIII group or metallic compounds may be used the -- the [VI group and/or] -- a VIII group's whole metallic-oxide concentration is 10 - 30 % of the weight ten to 40% of the weight eight to 40% of the weight advantageously three to 40% of the weight preferably one to 40% of the weight the -- the [to a VIII group's metal (or two or more carat group)] -- the weight ratio displayed by the metallic oxide of VI group's metal (or two or more carat group) -- 1.25-20 -- it is 2-10 preferably Furthermore, this catalyst contains phosphorus. Phosphorus oxide P2 O5 The phosphorus content displayed by concentration is less than 10 % of the weight preferably less than 15% of the weight.

[0049] the hydrogenation function (the -- the [a VIII group's metal or] -- the [VI group and] -- the oxide of a VIII group's metal should put together) defined previously may be introduced into a catalyst by various methods in the various level of manufacture

[0050] A part of this hydrogenation function may all be introduced at the time of kneading with the oxide gel which accepts it (in the case [The / VI group and] of the combination of the oxide a VIII group's metal), or is chosen as a matrix with bridge-like 2:1 JI octahedron phyllosilicate. the selected metal on the baking support which this hydrogenation function is distributed in the selected matrix, and consists of 2:1 JI octahedron phyllosilicate which is a bridge-like depending on the case -- the -- when it belongs to a VIII group, it may be introduced by the ion exchange operation of 1 time or multiple times using the solution containing the precursor salt of this metal this hydrogenation function -- the -- the case where the precursor of the oxide VI group's metal (especially molybdenum or a tungsten) is beforehand introduced at the time of kneading of support -- the -- it may be introduced by sinking-in operation of the 1 time or multiple times of the support calcinated and fabricated by the precursor solution of the oxide a VIII group's metal (especially cobalt and nickel) the last -- this hydrogenation function -- the -- the [VI group and/or] -- it may be introduced by sinking-in operation of the 1 time or multiple times of the baking support which consists of the bridge-like 2:1 JI octahedron phyllosilicate and the matrix by the solution containing the precursor of a VIII group's metallic oxide the -- the precursor of the oxide of a VIII group metal -- desirable -- the -- the [after the precursor of the oxide of VI group metal, or / these] -- the precursor of the oxide of VI group metal -- simultaneously, it is introduced

[0051] When a metaled oxide is introduced in two or more sinking-in processes of a corresponding precursor salt, the middle baking process of a catalyst must be performed at the temperature of 250-600 degrees C.

[0052] Sinking [of molybdenum] in may be promoted by addition of the phosphoric acid to the inside of the Para ammonium-molybdate solution.

[0053] Therefore, generally the acquired catalyst is used in conversion of a hydrocarbon, especially hydrogenation cracking. These catalysts show the selectivity improved about manufacture of a very quality middle cut in hydrogenation cracking as compared with the zeolite catalyst of the advanced technology.

[0054] The brewing raw materials used in this method are a gas oil, a reduced pressure gas oil, a deasphalting residue, hydrogen-treating finishing residues, or those equivalents. they may be heavy fractions which consist of at least 80 capacity [of a compound (namely, a carbon atomic number -- it corresponds to the compound which contains 15-20 even if few) with a boiling point of 350-580 degrees C] % Generally these heavy fractions contain sulfur and a hetero atom like nitrogen. A nitrogen content is usually the 1 - 5000 weight ppm. A sulfur content is 0.01 - 5 % of the weight. Temperature, a pressure, the recycle rate of hydrogen, and hydrogenation cracking conditions like [per hour] space velocity change sharply according to the facility installation used for the quality and the refiner of the kind of brewing raw material, and the request matter.

[0055] Generally temperature exceeds 230 degrees C and, in many cases, is less than 450 degrees C preferably 300-480 degrees C. Generally a pressure exceeds 2 or more MPa(s) of 3MPa(s), and furthers are 10MPa(s). The recycle rate of hydrogen is 100l. in the hydrogen minimum per 1l. of brewing raw materials. In many cases, it is 260-3000l. of hydrogen. Generally space velocity is 0.2-10h-1 per hour.

[0056]

[Embodiments of the Invention] Although the following example illustrates this invention, it does not limit the range at all.

[Example 1]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 42g of

0.75M, and the solution which consists of 150ml of distilled water. The whole was filtered after churning for 2 hours and 30 minutes at the room temperature, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 1.12g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for 30 minutes at the room temperature, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 29% at baking. Therefore, distance d001 between grids (periodicity) 29.5x10-10 The value of m (2.95nm) was reached. This sample had the tint of dark brown. Furthermore, it heat-treated at 650 degrees C under air for 4 hours, and oxidization by the whole organic substance was drawn. Weight loss at 500-650 degrees C was 9%. d001 of the matter 32.0x10-10 It is m (3.20nm) and the BET specific surface area is 2 577m. It was /g. It sets after baking of 4 hours at 750 degrees C under air, and the distance between grids (periodicity) is 41.8x10-10. It was m (4.18nm).

[0057] [Example 2]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 42g of 0.75M, and the solution which consists of 150ml of distilled water. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 0.56g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 25% at baking. Therefore, distance d001 between grids (periodicity) 37.8x10-10 The value of m (3.78nm) was reached. Furthermore, it heat-treated at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 6%. d001 of the matter 45.8x10-10 It is m (4.58nm) and the BET specific surface area is 2 500m. It was /g.

[0058] [Example 3]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 42g of 0.75M, and the solution which consists of 150ml of distilled water. The whole was filtered after churning for 2 hours and 30 minutes at the room temperature, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 0.56g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) Slurrying was carried out into the mixture which consists of 15.08g. The whole was filtered after churning for 30 minutes at the room temperature, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 22% at baking. Therefore, distance d001 between grids (periodicity) 27.7x10-10 The value of m (2.77nm) was reached. Furthermore, it processed at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 8.7%. d001 of the matter 30.4x10-10 It was m (3.04nm).

[0059] [Example 4]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 21g of 0.75M, and the solution which consists of 75ml of distilled water. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 0.56g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 24% at baking. Therefore, distance d001 between grids (periodicity) 41.3x10-10 The value of m (4.13nm) was reached. Furthermore, it heat-treated at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 8%. d001 of the matter 42.0x10-10 It is m (4.20nm) and the BET specific surface area is 2 518m. It was /g.

[0060] [Example 5]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into the chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 42g of 0.75M] solution. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 1.12g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 29% at baking. Therefore, distance d001 between grids (periodicity) 46.8x10-10 The value of m (4.68nm) was reached. Furthermore, it heat-treated at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 8%. d001 of the matter 40.1x10-10 It is m (4.01nm) and the BET specific surface area is 2 543m. It was /g. By baking at 750 degrees C of this sample performed behind, it is 37.2x10-10. d001 of m (3.72nm) The matter which it has arose.

[0061] [Example 6]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 13m of BET specific surface areas. Natural activation montmorillonite KSF which has /g Slurrying of the 1.5g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 21g of 0.75M, and the solution which consists of 75ml of distilled water. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 0.56g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 24% at baking. In this case, distance d001 between grids (periodicity) 37.2x10-10 The value of m (3.72nm) was reached. Furthermore, it heat-treated at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 6%. d001 of the matter 36.9x10-10 It is m (3.69nm) and the BET specific surface area is 2 506m. It was /g.

[0062] [Example 7]

Bridge-like montmorillonite Si/ZrProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation

montmorillonite K10 which has /g Slurrying of the 15g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 210g of 0.75M, and the solution which consists of 75ml of distilled water. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 2g of this sample. 1.12g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) 15.08g and isopropoxide zirconium Zr (OC3 H7) Slurrying was carried out into the mixture which consists of 0.59g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 650 degrees C under air for 4 hours. Successive weight loss was 26% at baking. Therefore, distance d001 between grids (periodicity) 43.6x10-10 The value of m (4.36nm) was reached. A BET specific surface area is 2 510m. It was /g.

[Translation done.]

TECHNICAL FIELD

[The technical field to which invention belongs] this invention is the nature activated, for example, or relates to the montmorillonite type 2:1 JI octahedron phyllosilicate obtained by composition. The aforementioned composition is performed into a fluoride medium to the bottom of existence of a hydrofluoric acid and/or another source of a fluoride anion depending on the case. the aforementioned phyllosilicate -- the shape (bridged) of a bridge it is -- and big distance between grids (interplanar spacing) It has. d001 The distance between grids expressed is the sum total of the thickness of a layer (sheet), and the space between layers.

[0002] Furthermore, this invention relates also to the manufacture method for obtaining the aforementioned phyllosilicate.

[0003] These phyllosilicate may be contained in the constituent of the catalyst used in hydrogenation cracking of a hydrocarbon brewing raw material.

[0004] further -- this invention -- for example, the activated nature -- namely, -- for example, or it was processed from the acid, depending on the case, it is compounded in a fluoride medium (under existence of a hydrofluoric acid and/or another source of a fluoride anion), and is related also with the catalyst containing at least one montmorillonite type 2:1 JI octahedron phyllosilicate [-izing / the shape of a bridge / subsequently / phyllosilicate] The aforementioned phyllosilicate has a big distance between grids (the distance between this grid is the sum total of the thickness of a layer (sheet sheet), and the space between layers (space between the sheets)). Furthermore, a catalyst contains at least one faujasite structured type zeolite Y with at least one matrix depending on the case. Furthermore, this invention relates also to the conversion method of a hydrocarbon brewing raw material of using this catalyst, especially the hydrogenation cracking method.

[Translation done.]

PRIOR ART

[Description of the Prior Art] Hydrogenation cracking of a heavy petroleum fraction is the very important method of petroleum refining, and it becomes possible to manufacture a light fraction like a gasoline, evaporation fuel, and a light gas oil by this refining method from the heavy brewing raw material of the surplus which does not almost have added value. A refiner searches for these light fractions in order to fit the manufacture to the need of a commercial scene. It is that the merit of catalytic hydrogenation cracking supplies a very quality middle cut, evaporation fuel (jet fuel), and a gas oil as compared with contact cracking. On the other hand, the generated gasoline has a low octane value considerably rather than the gasoline produced according to contact cracking.

[0006] The catalysts used in hydrogenation cracking are all dual-function [which combines an acid function and a hydrogenation function] type catalysts. An acid function is brought about with the combination of support, for example, a halogenation (especially chlorination or fluoridation) alumina, boron oxide, and aluminum, amorphous-silica alumina, and zeolite of a big specific surface area (generally 150-800m2 /g) which has surface acidity. a hydrogenation function -- the [element periodic-table] -- or it is based on one or more metal, for example, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmiums, iridium, and platinum of a VIII group -- the [or / element periodic-table] -- the [at least one metal of VI group, for example, chromium, molybdenum and a tungsten, and] -- it is brought with combination with at least one metal of a VIII group

[0007] The balance between the dual functions which are an acid function and a hydrogenation function is a fundamental parameter. The activity and selectivity of a catalyst are determined with this parameter. By the weak-acid function and the strong hydrogenation function, the catalyst which is hardly activity (the degree of subvital) is offered. These are equipped with the very high selectivity of a middle cut although these catalysts generally act at an elevated temperature (390 degrees C or more) with a low space speed of supply (VVH displayed to the capacity of the brewing raw material which should be processed per one unit of catalyst capacity is generally two or less per hour). On the contrary, although a very activity catalyst is offered by the strong acid function and the weak hydrogenation function, these show low selectivity in a middle cut. Therefore, it is possible by choosing each of these functions appropriately to adjust the lot of the activity/selectivity of a catalyst.

[0008] Therefore, it is one of the big merits of hydrogenation cracking to have big adaptability (flexibility) (flexibility), i.e., the adaptability about the catalyst used, in some level. The adaptability (flexibility) of the brewing raw material which should be processed about the obtained matter with this adaptability (flexibility) is brought about. The parameter with easy controlling is the acidity of a catalyst support.

[0009] The conventional catalytic hydrogenation cracking catalyst consists of support which is acescence, for example, an amorphous-silica alumina, in the most. In order to manufacture a very quality middle cut, these systems are further used, in order that the acidity may manufacture stock oil to a low case very much.

[0010] An amorphous-silica alumina is acescence support. the hydrogenation cracking catalyst of a large number in a commercial scene -- the -- the case where the content of the hetero atom poison (for example, S, N, and a heavy metal) of the silica alumina combined with a VIII group's metal or the brewing raw material which should be processed exceeds 0.5 % of the weight preferably -- the -- VIB the [a group and] -- it consists of silica aluminas combined with the combination of the sulfide a VIII group's metal These systems have the very high selectivity of a middle cut. The generated matter has high quality. Furthermore, it is also most possible among those catalysts for such a catalyst to manufacture lubricous stock oil about the thing of the acescence. It is the weak activity un-arranging [of all these catalyst systems that use amorphous support as the base], as mentioned already.

[0011]

[Elements of the Invention] A bird clapper came [by the research achievements performed by these people, / although it was not expecting / in the catalyst containing at least one montmorillonite type 2:1 JI octahedron phyllosilicate / improving the performance in hydrogenation cracking as compared with the well-known catalyst in the advanced technology] to be proved possible. Depending on the natural phyllosilicate activated namely, processed from the acid, or the case, this JI octahedron phyllosilicate is compounded in a fluoride medium (under existence of hydrofluoric-acid HF and/or another source of a fluoride anion), subsequently are-izing [phyllosilicate / the shape of a bridge] (method preferably indicated by this specification), and it is combined with the zeolite Y of a faujasite structured type depending on the case.

[0012] In accuracy, this invention is d001 of at least 2.0x10 to 9 m more. . the distance between grids expressed -- having -- and SiO2 aluminum2 O3 TiO2 ZrO2 And V2 O5 from -- it is related with the montmorillonite type 2:1 JI octahedron phyllosilicate which contains the pillar (pillar) which uses all combination of at least one compound in the compound chosen from the becoming group, or these compounds as the base in the space between layers desirable -- phyllosilicate -- pillar SiO2 or it contains -- otherwise, SiO2 aluminum2 O3 TiO2 ZrO2 And V2O5 from -- the pillar which uses combination with at least one compound in the compound chosen from the becoming group as the base is included Depending on the case, this phyllosilicate contains a fluorine.

[0013] According to this invention (put under existence of hydrofluoric-acid HF and/or another source of a fluoride anion in a fluoride medium depending on the case.) These bridge-like 2:1 JI octahedron phyllosilicate prepared beforehand is the distance d001 between grids which exceeds 2.8x10 to 9 m more preferably, or exceeds further 3.0x10 to 9 m at least 2.65x10 to 9 m preferably at least 2.0x10 to 9 m. It has. Especially the distance of at least 3.3x10 to 9 m is a pillar SiO2. Or pillar SiO2 It obtains and gets in an oxide besides +. Generally 6.0x10 - 9 or less m of distance between this grid is 5.0x10 - 9 or less m preferably. d001 The distance between grids displayed expresses the sum total of the thickness of a layer (sheet), and the space between layers. Using the conventional powder X-ray diffractometry (orientated) by which orientation was carried out, this value is acquired directly and it deals in it.

[0014] Furthermore, this invention relates to the manufacture method of the aforementioned phyllosilicate. In this method, after making

phyllosilicate into the letter of suspension into the solution of a surfactant and separating a solid-state from this solution subsequently, this phyllosilicate is contacted with the mixture containing the 1st or 2nd at least one amine and at least one alkoxide of the element chosen from the group which consists of Si, aluminum, Zr, Ti, and V. Preferably, at least one silicon alkoxide is used with at least one alkoxide of the element chosen from the group which consists of aluminum, Zr, Ti, and V depending on the case.

[0015] 2:1 JI octahedron phyllosilicate is a mineral produced by the pile of an element-like layer (sheet). Although the chemical bond between the elements of phyllosilicate structure is ion covalent bond, it is assumed that these chemical bonds are ionicity in order to make this specification simple.

[0016] It is possible to acquire the field which has the hexagon-like cavity (cavity) called hexagon-like side by removing one ion O2- from two arrays of ion O2- from the display which ion O2- touches mutually in a flat surface.

[0017] The structure of FIRAITO is the hexagon-like side of ion O2-, and ion O2- and ion OH-. It is briefly expressed by arrangement with a compact side, and gets by it. The cavity of the hexagon-like side of ion O2- is filled by ion OH-. By the superposition of two compact sides into which both sides were inserted by the hexagon-like side, between two tetrahedral layers (T), it becomes possible to demarcate an octahedral layer (O), and naming of Layer (sheet) TOT originates from this.

[0018] It becomes possible to demarcate the field which has the octahedron cavity located in the octahedral layer between two fields which have a tetrahedron cavity, and such arrangement similarly named 2:1 enables it to demarcate one field in a fourth page each body whorl. Four face pieces each have an octahedral layer and shared ion O2-. Other three each of ion O2- is shared with another tetrahedron of the same tetrahedral layer.

[0019] Therefore, a crystal unit lattice becomes each side from six octahedron cavities which have four tetrahedron cavities. It is the formula Si 8 with such arrangement ideal in FIRAITO which consists of elements Si, aluminum, O, and H. (aluminum4 **2) O20 (OH) 4 It is in agreement. Although a tetrahedron cavity contains an aluminum element including a silicon element in a JI octahedron cavity, one [in / three octahedron cavities / in this case] is empty (**). Such an assembly is electrically neutral. In many cases, a half-unit lattice is used. This is formula:.

[Formula 1]

$$Si_4(Al_2\tilde{y})O_{10}(OH)_2$$

It ****.

[0020] In the case of montmorillonite type phyllosilicate, an octahedron aluminum element is replaced in part with a divalent element. This substitution gives an organization negative charge. This needs existence of the exchangeable compensation cation located in the space between layers. It depends for the thickness of the space between layers on the kind and its hydration state of a compensation cation. Furthermore, this space can hold other chemical species, such as water, an amine, a salt, alcohol, and a base.

[0021] The phyllosilicate by this invention is montmorillonite type 2:1 JI octahedron phyllosilicate which has the feature mentioned later. In these phyllosilicate, a pillar is introduced in the space between layers (a pillar is chosen from SiO2 , aluminum2 O3 , TiO2 , ZrO2 , and V2 O5), and it is the distance d001 between [of at least 2.0x10 to 9 m] grids. It is made to be generated.

[0022] The general (as opposed to half-unit lattice) chemical formula of the start montmorillonite type 2:1 JI octahedron phyllosilicate before shape[of a bridge]-izing (bridging) is : which is as follows. [Formula 2]

$$M^{m+}_{x/m}\,(Si_4\,(T_{(2-x)}Mg_x\tilde{y})\,O_{10}\,(OH)_{(2-y)}\,F_y)^{x-}$$

inside of formula, and -T -- the -- the element (for example, B, aluminum, Ga) chosen from the group which consists of an IIIA group's element and iron, manganese, chromium, titanium, and vanadium are expressed

[0023] - M -- the -- the [IA group and] -- IIA the [a group and] -- it is at least one compensation cation chosen from the group which consists of the cation of a VIII group's element, the organic cation containing nitrogen, an ammonium cation, and a rare earth cation When montmorillonite type 2:1 JI octahedron phyllosilicate is obtained by composition, it is generated from a reaction medium or a cation is introduced by at least one exchange method. Advantageously, the cation produced from a reaction medium is chosen from the group which consists of alkali (except for a lithium), an ammonium cation (NH4+), an organic cation (alkylammonium and aryl ammonium are included) containing nitrogen, and an organic cation (an alkyl phosphonium and an aryl phosphonium are included) containing phosphorus. You may be the compensation cation introduced by the ion exchange on the natural montmorillonite which also depended M on the post-composition ion exchange, or was activated depending on the case. this cation M -- the [of an element periodic table] -- the [IA group and] -- IIA the [a group and] -- it is chosen out of the group which consists of the cation of a VIII group's element, the cation (cation of the element of the atomic numbers 57-71 (71 is contained)) of rare earth, an organic cation (alkylammonium and aryl ammonium are included) containing nitrogen, and an ammonium cation

[0024] - m is the valence of Cation M.

[0025] - x is more greatly [than 0] smaller than 2 -- it is the number of 0.1-0.8 preferably

[0026] - y is the number of 0-2. When phyllosilicate contains a fluorine, y is larger than 0.

[0027]

[Formula 3]

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the 2:1 JI octahedron phyllosilicate used in the state of nature -- desirable -- the temperature of 20-200 degrees C, and an ordinary-pressure -20 bar pressure -- it is -- for example, HNO3 HCl and H2SO4 H3 PO4 etc. -- acid treatment is used for example, activated

[0028] The X diffraction chart of the 2:1 JI octahedron phyllosilicate before shape[of a bridge]-izing is : and (1.49**0.01) x10-10 characterized by existence of the following spectral line. d060 of m The characterized spectral line.

[0029] - d001 At least one reflection 001 which is x(1.25**0.3)10-9m according to the kind of compensation cation, and its hydration state in the humidity examined.

[0030] : and 2:1 JI octahedron phyllosilicate are made into the letter of suspension into the solution of the surfactant which has preferably 0.01-1 mol /of concentration within the limits of 0.05-0.7 mols/l. l. [-izing / the shape of a bridge / with the way these 2:1 JI octahedron phyllosilicate includes the following process / phyllosilicate] If there is no usable surfactant as if in this process in an anionic surfactant like an alkyl sulfate and an alkyl sulfonate as an example which is not limited, for example, it is a cation nature surfactant. As for halogenation, a tetraalkylammonium hydroxide, for example, chlorination cetyl trimethylammonium, or a further, the alkylammonium compound of the

gemination is mentioned as a cation nature surfactant.
[0031] as an example -- bromination -- hexadecyl trimethylammonium, ethyl-bromide hexadecyl dimethylannmonium, and bromination -- octadecyl trimethylammonium, a dodecyltrimethylammonium bromide, and bromination -- didodecyl dimethylannmonium is usable Furthermore, you may use the neutral surfactant X-100, for example, a triton, or a polyethylene oxide (POE).
[0032] As for the whole, a medium is filtered after 5 minutes - 12 hours and the contact time agitated more preferably for 15 minutes to 3 hours for 15 minutes to 6 hours, and subsequently it is washed by distilled water, and, subsequently to the bottom of air or inert gas, finally, dries preferably at the temperature of 40-150 degrees C for 30 minutes to 12 hours for 5 minutes to 24 hours.
[0033] When phyllosilicate is not an ammonium gestalt, this phyllosilicate mainly obtains the 2:1 JI octahedron phyllosilicate of an ammonium gestalt to this contractor, beforehand in response to the fact that all well-known processings. As an example to which the processing for performing this conversion is not limited, the ion exchange by the solution of an ammonium salt (an ammonium nitrate and/or ammonium chloride) is mentioned.
[0034] - 2:1 JI octahedron phyllosilicate processed by the operating instruction subsequently to a precedence process indicated, :i contacted into the mixture containing the following At least one RNH2 Type primary amine, or the R'RNH type 2nd amine (in here, R and R' is chosen from the group which consists of the carbon content machine which may have the carbon atomic numbers 1-16 which are advantageously replaced by other bases or are not replaced, an alkyl group, an isoalkyl group, a NAFUTENIRU machine, and an aromatic machine).
[0035] ii) Mixture of at least one alkoxide of an element, or an alkoxide. An element is chosen from the group which consists of silicon, aluminum, a zirconium, titanium, and vanadium. This alkoxide is shown by general formula M(OR) n (M is the above-mentioned element among a formula, n is the valence of the aforementioned element, and R is a basis advantageously chosen from the group which consists of substitution or an unsubstituted alkyl group, an isoalkyl group, a NAFUTENIRU machine, and an aromatic machine).
[0036] various basis-OR is the same according to the kind of R group chosen from the group defined above -- or you may differ
[0037] Contact neglect of the whole is preferably carried out under churning for 5 minutes to 8 hours for 5 minutes to 12 hours.
[0038] iii Subsequently, the 2:1 JI octahedron phyllosilicate [-izing / the shape of a bridge / in this way / phyllosilicate] is filtered, and, subsequently to the bottom of air or inert gas, is preferably dried at the temperature of 40-150 degrees C for 30 minutes to 12 hours for 5 minutes to 24 hours.
[0039] Habitually, after dryness, advantageously, phyllosilicate raises temperature and is given to baking. Temperature may rise at 400-800 degrees C more advantageously by 300-800 degrees C preferably to 800 degrees C. A firing time is changed. Generally temperature is maintained preferably for 4 to 8 hours for 1 to 10 hours. Subsequently, the solid-state is made to cool.
[0040] this shape-ized method of a bridge -- SiO2 aluminum2 O3 TiO2 ZrO2 and V2 O5 it is -- it becomes possible to introduce the mixture of a pillar or these pillars quickly simply in the space between layers of 2:1 JI octahedron phyllosilicate
[0041] In relation to the 2:1 JI octahedron phyllosilicate before shape[of a bridge]-izing, the phyllosilicate by this invention has the spectrum of an X diffraction. Therefore, it is at least 2.0x10-10 by this spectrum. Distance d001 between grids which increases to the value of m clearly It becomes possible to calculate. further -- specific surface area -- general -- 200-1000m2 /g -- desirable -- 250-700m2 Increasing to /g is admitted. Line d060 of an X diffraction spectrum It is held.
[0042] Furthermore, this invention has the distance between [of at least 2.0x10 to 9 m] grids. and SiO2 aluminum2 O3 TiO2 ZrO2 And V2 O5 from -- at least one compound in the compound chosen from the becoming group -- Or depending on the case, it is related also with the catalyst which contains Zeolite Y with at least one montmorillonite type 2:1 JI octahedron phyllosilicate containing the pillar (as [indicated / previously]) which uses all combination of these compounds as the base, and at least one matrix. desirable -- this phyllosilicate -- at least -- pillar SiO2 or it contains -- or SiO2 aluminum2 O3 TiO2 ZrO2 And V2 O5 from -- the pillar which uses combination with at least one compound in the compound chosen from the becoming group as the base is included
[0043] the catalyst of this invention -- the faujasite structured type zeolite Y (Zeolite Molecular Sieves Structure, Chemistry and Uses, D.W.BRECK, J.WILLEY and Sons 1973) -- especially -- lattice-parameter (24.24-24.55) x10-10 The dealuminization zeolite Y of m may be included. The stabilization zeolite Y generally [the gestalt preferably exchanged in part at least among the usable zeolites Y using a metal cation, for example, an alkaline-earth-metal cation, and/or the rare-earth-metal cation of the atomic numbers 57-71 (71 is contained) or a hydrogen type gestalt] called hyperstability zeolite, i.e., USY, is used.
[0044] :SiO2 characterized by the various specification that acid type zeolite H-Y is especially advantageous and /aluminum2 O3 mole ratios 8-70 -- desirable -- about 12-40 Less than 0.15% of the weight of the sodium content measured about the zeolite calcinated at 1100 degrees C. lattice parameter 24.55x10-10 of an element-like unit lattice m to 24.24x10-10 m -- desirable -- 24.38x10-10 m to 24.26x10-10 m. Incorporation capacity CNa of the sodium ion exceeding about 0.85 which is reformed, and it is carbonated and is displayed with the number of grams of Na per [which was subsequently calcinated] 100g of zeolites. B.E.T. about 400 measured by law -- m2 /g is exceeded -- desirable -- 550m2 Specific surface area exceeding /g. Steam adsorption capacity exceeding about 6% with a temperature [in the partial pressure of 2.6 torrs (namely, 34.6MPa(s))] of 25 degrees C. Diameter 20x10-10 m to 80x10-10 It is with 5 - 40% preferably the 5 - 45% of the total pore volume of the zeolite contained in the pore of m. Diameter 80x10-10 Generally [exceed m and] it is 1000x10-10. The 5 - 45% of the total pore volume of the zeolite contained in the pore of under m, 5 - 40% is included preferably, and the remainder of pore volume is a diameter 20x10-10. Pore distribution which is included in the pore of under m and which is measured by physical adsorption of nitrogen.
[0045] Furthermore, the catalyst of this invention includes at least one amorphous substance or imperfect-crystal-ized (low crystallinity) matrix chosen from the group which usually consists of an alumina, a silica, a magnesium oxide, titanium oxide, a zirconium oxide, an aluminum phosphate, phosphoric acid titanium or a zirconium phosphate, boron oxide, combination of at least two compounds in these compounds, and combination of an alumina and boron oxide, for example.
[0046] A matrix is chosen from the group which consists of combination of a silica, an alumina, a magnesium oxide, and a silica alumina, and combination of a silica and a magnesium oxide preferably.
[0047] Therefore, the catalyst of this invention is a. 1 - 80% of at least one bridge-like 2:1 JI octahedron phyllosilicate and a further are 15 - 50 % of the weight more preferably ten to 60% of the weight four to 70% of the weight. b) It is at least one hydrogen type faujasite structure zeolite Y which has the desirable above-mentioned feature. It is [0 (namely, 0.1) - 10 % of the weight, and] c more preferably zero (namely, 0.1) to 20% of the weight zero (namely, 0.1) to 30% of the weight. At least one matrix defined previously 1 - 99 % of the weight is included.
[0048] The catalyst of this invention may be prepared by this contractor by all well-known methods. One of the desirable methods in this

invention consists of fabricating an extrusion object with a diameter of 0.4-4mm through the paste which Zeolite Y was made to knead for dozens of minutes with bridge-like 2:1 JI octahedron phyllosilicate in a humid alumina gel, and was subsequently obtained in this way in to a die depending on the case. Subsequently, preferably, with room temperature -250 degree C temperature, generally a catalyst is calcinated at the temperature of about 250-600 degrees C, after drying with a drying furnace. Furthermore, generally, this catalyst contains at least one catalyst element like the metal which has for example, hydrogenation and a dehydrogenation function. general -- hydrogenation and a dehydrogenation function -- the [for example, / like especially nickel and cobalt] -- it is secured with a VIII group's at least one metal or metallic compounds the [of an element periodic table] -- the [at least one metal (especially molybdenum or a tungsten) of VI group or metallic compounds, and] -- combination with at least one metal (especially cobalt or nickel) of a VIII group or metallic compounds may be used the -- the [VI group and/or] -- a VIII group's whole metallic-oxide concentration is 10 - 30 % of the weight ten to 40% of the weight eight to 40% of the weight advantageously three to 40% of the weight preferably one to 40% of the weight the -- the [to a VIII group's metal (or two or more carat group)] -- the weight ratio displayed by the metallic oxide of VI group's metal (or two or more carat group) -- 1.25-20 -- it is 2-10 preferably Furthermore, this catalyst contains phosphorus. Phosphorus oxide P2 O5 The phosphorus content displayed by concentration is less than 10 % of the weight preferably less than 15% of the weight.

[0049] the hydrogenation function (the -- the [a VIII group's metal or] -- the [VI group and] -- the oxide of a VIII group's metal should put together) defined previously may be introduced into a catalyst by various methods in the various level of manufacture

[0050] A part of this hydrogenation function may all be introduced at the time of kneading with the oxide gel which accepts it (in the case [The / VI group and] of the combination of the oxide a VIII group's metal), or is chosen as a matrix with bridge-like 2:1 JI octahedron phyllosilicate. the selected metal on the baking support which this hydrogenation function is distributed in the selected matrix, and consists of 2:1 JI octahedron phyllosilicate which is a bridge-like depending on the case -- the -- when it belongs to a VIII group, it may be introduced by the ion exchange operation of 1 time or multiple times using the solution containing the precursor salt of this metal this hydrogenation function -- the -- the case where the precursor of the oxide VI group's metal (especially molybdenum or a tungsten) is beforehand introduced at the time of kneading of support -- the -- it may be introduced by sinking-in operation of the 1 time or multiple times of the support calcinated and fabricated by the precursor solution of the oxide a VIII group's metal (especially cobalt and nickel) the last -- this hydrogenation function -- the -- the [VI group and/or] -- it may be introduced by sinking-in operation of the 1 time or multiple times of the baking support which consists of the bridge-like 2:1 JI octahedron phyllosilicate and the matrix by the solution containing the precursor of a VIII group's metallic oxide the -- the precursor of the oxide of a VIII group metal -- desirable -- the -- the [after the precursor of the oxide of VI group metal, or / these] -- the precursor of the oxide of VI group metal -- simultaneously, it is introduced

[0051] When a metaled oxide is introduced in two or more sinking-in processes of a corresponding precursor salt, the middle baking process of a catalyst must be performed at the temperature of 250-600 degrees C.

[0052] Sinking [of molybdenum] in may be promoted by addition of the phosphoric acid to the inside of the Para ammonium-molybdate solution.

[0053] Therefore, generally the acquired catalyst is used in conversion of a hydrocarbon, especially hydrogenation cracking. These catalysts show the selectivity improved about manufacture of a very quality middle cut in hydrogenation cracking as compared with the zeolite catalyst of the advanced technology.

[0054] The brewing raw materials used in this method are a gas oil, a reduced pressure gas oil, a deasphalting residue, hydrogen-treating finishing residues, or those equivalents. they may be heavy fractions which consist of at least 80 capacity [of a compound (namely, a carbon atomic number -- it corresponds to the compound which contains 15-20 even if few) with a boiling point of 350-580 degrees C] % Generally these heavy fractions contain sulfur and a hetero atom like nitrogen. A nitrogen content is usually the 1 - 5000 weight ppm. A sulfur content is 0.01 - 5 % of the weight. Temperature, a pressure, the recycle rate of hydrogen, and hydrogenation cracking conditions like [per hour] space velocity change sharply according to the facility installation used for the quality and the refiner of the kind of brewing raw material, and the request matter.

[0055] Generally temperature exceeds 230 degrees C and, in many cases, is less than 450 degrees C preferably 300-480 degrees C. Generally a pressure exceeds 2 or more MPa(s) of 3MPa(s), and furthers are 10MPa(s). The recycle rate of hydrogen is 100l. in the hydrogen minimum per 1l. of brewing raw materials. In many cases, it is 260-3000l. of hydrogen. Generally space velocity is 0.2-10h-1 per hour.

[0056]

[Embodiments of the Invention] Although the following example illustrates this invention, it does not limit the range at all.

[Example 1]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 42g of 0.75M, and the solution which consists of 150ml of distilled water. The whole was filtered after churning for 2 hours and 30 minutes at the room temperature, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 1.12g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for 30 minutes at the room temperature, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 29% at baking. Therefore, distance d001 between grids (periodicity) 29.5x10-10 The value of m (2.95nm) was reached. This sample had the tint of dark brown. Furthermore, it heat-treated at 650 degrees C under air for 4 hours, and oxidization by the whole organic substance was drawn. Weight loss at 500-650 degrees C was 9%. d001 of the matter 32.0x10-10 It is m (3.20nm) and the BET specific surface area is 2 577m. It was /g. It sets after baking of 4 hours at 750 degrees C under air, and the distance between grids (periodicity) is 41.8x10-10. It was m (4.18nm).

[0057] [Example 2]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 42g of 0.75M, and the solution which consists of 150ml of distilled water. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 0.56g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was

carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 25% at baking. Therefore, distance d001 between grids (periodicity) 37.8x10-10 The value of m (3.78nm) was reached. Furthermore, it heat-treated at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 6%. d001 of the matter 45.8x10-10 It is m (4.58nm) and the BET specific surface area is 2 500m. It was /g.

[0058] [Example 3]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 42g of 0.75M, and the solution which consists of 150ml of distilled water. The whole was filtered after churning for 2 hours and 30 minutes at the room temperature, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 0.56g and tetraethyl ortho silicic-acid ethyl Si 4 (OC2 H5) Slurrying was carried out into the mixture which consists of 15.08g. The whole was filtered after churning for 30 minutes at the room temperature, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 22% at baking. Therefore, distance d001 between grids (periodicity) 27.7x10-10 The value of m (2.77nm) was reached. Furthermore, it processed at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 8.7%. d001 of the matter 30.4x10-10 It was m (3.04nm).

[0059] [Example 4]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 21g of 0.75M, and the solution which consists of 75ml of distilled water. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 0.56g and tetraethyl ortho silicic-acid ethyl Si 4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 24% at baking. Therefore, distance d001 between grids (periodicity) 41.3x10-10 The value of m (4.13nm) was reached. Furthermore, it heat-treated at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 8%. d001 of the matter 42.0x10-10 It is m (4.20nm) and the BET specific surface area is 2 518m. It was /g.

[0060] [Example 5]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 3g was carried out into the chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 42g of 0.75M] solution. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8</SUB> H17NH2) in 1g of this sample. 1.12g and tetraethyl ortho silicic-acid ethyl Si 4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 29% at baking. Therefore, distance d001 between grids (periodicity) 46.8x10-10 The value of m (4.68nm) was reached. Furthermore, it heat-treated at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 8%. d001 of the matter 40.1x10-10 It is m (4.01nm) and the BET specific surface area is 2 543m. It was /g. By baking at 750 degrees C of this sample performed behind, it is 37.2x10-10. d001 of m (3.72nm) The matter which it has arose.

[0061] [Example 6]

Bridge-like montmorillonite SiProlabo It is supplied by the shrine and is 2 13m of BET specific surface areas. Natural activation montmorillonite KSF which has /g Slurrying of the 1.5g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 21g of 0.75M, and the solution which consists of 75ml of distilled water. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 1g of this sample. 0.56g and tetraethyl ortho silicic-acid ethyl Si 4 (OC2 H5) Slurrying was carried out into the mixture which consists of 7.54g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 500 degrees C under air for 4 hours. Successive weight loss was 24% at baking. In this case, distance d001 between grids (periodicity) 37.2x10-10 The value of m (3.72nm) was reached. Furthermore, it heat-treated at 650 degrees C under air for 4 hours. Weight loss at 500-650 degrees C was 6%. d001 of the matter 36.9x10-10 It is m (3.69nm) and the BET specific surface area is 2 506m. It was /g.

[0062] [Example 7]

Bridge-like montmorillonite Si/ZrProlabo It is supplied by the shrine and is 2 257m of BET specific surface areas. Natural activation montmorillonite K10 which has /g Slurrying of the 15g was carried out into chlorination hexadecyl trimethylammonium (C16 TMA-Cl) 210g of 0.75M, and the solution which consists of 75ml of distilled water. The whole was filtered after churning for [in a room temperature] 2 hours and 30 minutes, 200ml distilled water washed, and, subsequently it was made to dry at 60 degrees C for 8 hours. Subsequently, it is an octyl amine (C8 H17NH2) in 2g of this sample. 1.12g and tetraethyl ethyl-orthosilicate Si4 (OC2 H5) 15.08g and isopropoxide zirconium Zr (OC3 H7) Slurrying was carried out into the mixture which consists of 0.59g. The whole was filtered after churning for [in a room temperature] 30 minutes, and, subsequently direct drying was carried out at 60 degrees C for 8 hours. Subsequently, the matter was calcinated at 650 degrees C under air for 4 hours. Successive weight loss was 26% at baking. Therefore, distance d001 between grids (periodicity) 43.6x10-10 The value of m (4.36nm) was reached. A BET specific surface area is 2 510m. It was /g.

[Translation done.]